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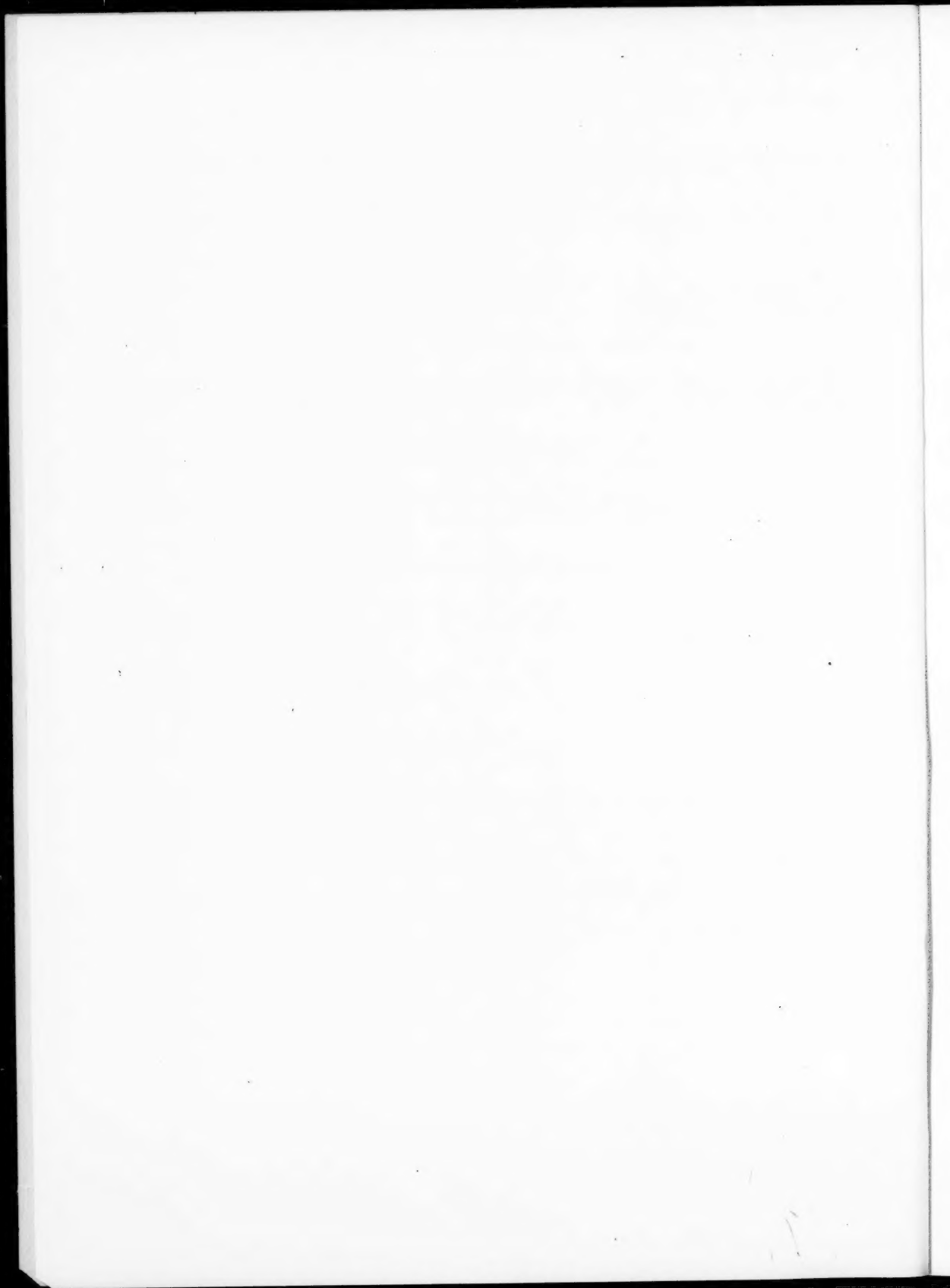
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THE MECHANISM OF ORGANOMERCURIAL OXIDATION BY MERCURIC SALTS^{1,2}

J. H. ROBSON AND GEORGE F. WRIGHT

ABSTRACT

It has been shown that the oxidation of organomercuric salts by inorganic mercuric salts is inhibited by oxygen, accelerated to some extent by acids, and will form esters as products even in the presence of much water. Moreover, the system will polymerize acrylonitrile. These evidences of free radical participation are substantiated by the formation of the same products when pernitrous acid replaces inorganic mercuric salt in the system. Kinetic studies show that radicals are involved in a self-regenerating chain in which active monomeric mercurous salt seems to be the carrier.

It has been shown previously (1) that the oxidation of organomercuric salts in which the anion is nitrate is much more facile than maintains for systems in which the salts are acetates. Because of this difference in reactivity we have found it convenient to discuss the nitrate and acetate systems separately.

THE OXIDATION OF ORGANOMERCURIC NITRATES

In the earlier publication (1) it was shown that the reaction of benzylmercuric nitrate with mercuric nitrate in methanol led to benzyl methyl ether and benzyl nitrate. Additional examples have now been sought. Although *n*-butylmercuric nitrate will not react, cyclohexylmercuric nitrate in methanol containing mercuric nitrate gives an 8% yield of methoxycyclohexane and a 31% yield of cyclohexyl nitrate.

Of greater interest is the observation that benzylmercuric nitrate with mercuric nitrate in water yields not only benzyl alcohol, benzaldehyde, and benzoic acid but also benzyl nitrate. Similarly cyclohexylmercuric nitrate with mercuric nitrate in water gives not only a 40% yield of cyclohexanol and a trace of formylcyclopentane (to be explained in a forthcoming publication) but also a 21% yield of cyclohexyl nitrate. The formation of these nitrate esters in aqueous solution is unusual even though these reaction systems are not entirely homogeneous. To be sure benzylmercuric chloride has been found (2) to yield benzyl nitrite and nitrate in nitric acid but little water was present in that system. Certainly cyclohexanol with mercuric nitrate in dilute nitric acid does not form cyclohexyl nitrate according to infrared spectral examination. Indeed the formation of appreciable amounts of nitrate esters under conditions where they should be absent or minimal if they were constituents of heteropolar or ionic equilibria indicates strongly that these nitrate esters are formed by a homopolar or free-radical mechanism.

¹Manuscript received July 16, 1959.

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario.

²Presented at the 136th meeting of the American Chemical Society, Atlantic City, 1959.

Of course the generality of the reaction whereby organomercuric nitrates are oxidized by mercuric nitrate is not established by the reactions in aqueous solutions, especially since the second-order kinetics of the non-aqueous reaction (1) cannot be demonstrated in the aqueous systems because of their inhomogeneity. Therefore, direct evidence for the participation of radicals in the methanolic systems has been sought. In the first instance this investigation has involved methanolic mercuric nitrate alone.

It has been shown by Waters and Merz (3, 4) and by Uri (5) that mercuric salts are reduced to the mercurous state in aqueous sulphuric acid containing various organic substrates when Fenton's reagent (6, 7) is added. The significance of the substrate is shown by the absence of reduction when mercuric nitrate in aqueous solution is treated with Fenton's reagent. As was expected, we find that methanolic mercuric nitrate is rapidly reduced to the mercurous level when hydrogen peroxide is added, if, also, a trace of ferrous salt is present. Methanolic mercuric nitrate also is reduced to mercurous nitrate when isobutyryl peroxide is added. The mercurous salt is quite stable in these media and metallic mercury is never detected.*

The reduction of mercuric to mercurous nitrate implies oxidation of the methanolic medium. Since the over-all reaction of mercuric nitrate with an organomercuric nitrate causes oxidation of the latter, it is reasonable to presume that reduction of the inorganic salt forms free radicals from the substrate which in turn act upon the organomercurial. In order to test this presumption we have treated alkylmercuric nitrates (which are stable toward demercuration in acids) with a peracid instead of mercuric nitrate. Although *n*-butylmercuric nitrate is so inert under these conditions that eventual reaction does not lead to recognizable products, we have been successful with cyclohexylmercurials.

Thus pernitrous acid (8, 9, 10, 11) is formed from sodium nitrite and hydrogen peroxide in aqueous medium. When cyclohexylmercuric nitrate is added to this system (together with some methanol for solubilization) mercurous salt is formed. The mercurous salt yield (52%) is not meaningful because Hg^+ is partly oxidized by this medium but it indicates that accompanying radicals are involved in the 30% yield of cyclohexanol and the 25% yield of cyclohexyl nitrate, which are obtained together with some cyclohexanone.

FORMATION AND PERSISTENCE OF RADICALS IN THE MERCURIC NITRATE-ORGANOMERCURIC NITRATE SYSTEM

Although a radical source such as pernitrous acid will convert cyclohexylmercuric nitrate to cyclohexanol and its nitrate ester, and Fenton's reagent will reduce mercuric nitrate in a manner which should produce radicals in and from the substrate, it remains to prove that radicals are formed and do persist in the actual system of organomercuric salt and inorganic mercuric salt.

There is some evidence that the initiation of the radical reaction may arise in the organomercurial itself, since a methanol solution of diphenylpicrylhydrazyl is bleached by each of a series of organomercuric nitrates. When the mercurial is present in large excess the bleaching of the hydrazyl proceeds at a first-order rate (Fig. 1). A series of such hydrazyl bleaching rates are shown in Table I together with the second-order rates for reaction of the same mercurials with mercuric nitrate. It may be seen that there is a rough correlation. Complete agreement cannot be expected because the first-order rate of hydrazyl bleaching would only be the first, inducing, step in the reactions that comprise

*It may be noted that mercuric acetate is not reduced under comparable conditions. Of course a complete reduction would not be expected since mercurous acetate is oxidized by peroxides. However, in the absence of any reduction one recalls Waters' observation that a radical chain reaction does not ordinarily proceed via acetato radicals.

the second-order oxidation. Nevertheless, the correspondence in relative rates for 6 of 10 entries in this table indicates that radicals are involved in the second-order oxidation.*

If radicals are involved in the oxidation of organomercuric nitrates by mercuric nitrate then these radicals ought to be detectable. To this end we first prepared 2-hydroxycyclohexylmercuric nitrate *in situ* by treatment of cyclohexene with 1 equivalent of mercuric

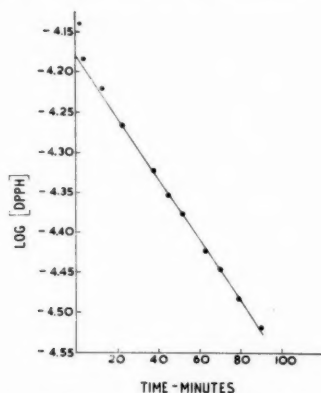


FIG. 1. The reaction of benzylmercuric nitrate (0.01 *M*) and diphenylpicrylhydrazyl (0.000081 *M*) in methanol at 25° C.

TABLE I
Comparison of reaction rates of nitratomercurials with diphenylpicrylhydrazyl and with mercuric nitrate

Nitratomercurial	1st order DPPH reaction ($k \times 10^3$)	2nd order oxidation reaction ($k \times 10^2$)
1. α -1-Nitratomercuri-2-methoxy-1,2-diphenylethane	21.4	30.0
2. Cyclohexylmercuric nitrate	17.1	2.11
3. Benzylmercuric nitrate	8.85	1.79
4. Isopropylmercuric nitrate	7.60	1.79
5. β -2-Methoxycyclohexylmercuric nitrate	3.03	— ^a
6. <i>n</i> -Propylmercuric nitrate	2.78	— ^a
7. α -2-Methoxycyclohexylmercuric nitrate	2.66	0.055
8. <i>n</i> -Butylmercuric nitrate	2.63	— ^a
9. 1-Phenyl-1-nitratomercuri-2-methyl-2-methoxypropane	2.44	1.74
10. β -1-Nitratomercuri-2-methoxy-1,2-diphenylethane	0.76	1.47

^a Too slow to be measured.

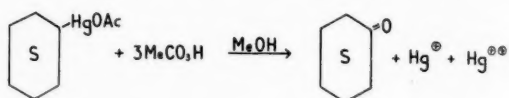
*It is of interest that since submission of this manuscript a monomeric mercurous salt has been postulated (Weinmayer, V. J. Am. Chem. Soc. **81**, 3590 (1959)) as an intermediate in the photolysis of oxyalkylmercuric halides. The specificity of methanol or water as the substrate is reminiscent of the reactions which we have described in the present publication. Moreover the coupling reaction which Weinmayer describes must have been preceded by a homolytic fission into radicals the presence of which are implied in any explanation of the hydrazyl bleaching reaction.

nitrate in aqueous solution and then added acrylonitrile. No polymer was formed during 24 hours. On the other hand, when another equivalent of mercuric nitrate was added together with the polyacrylonitrile polyarylonitrile, the system became turbid after 40 minutes and a 4% yield of acrylonitrile was obtained after 3 hours. Moreover, the turbidity appeared immediately and the yield of polymer was 7% when the system was deaerated before addition of mercuric nitrate and acrylonitrile. Finally the yield of polymer was increased to 24% by inclusion of 4 mole per cent of *N,N'*-methylene-bis-acrylamide as a cross-linking agent. These yields of polyacrylonitrile (with characteristically diffuse X-ray diffraction pattern) persuade us (12) that radical-induced polymerization has occurred, especially since the same behavior was observed with acrylonitrile and Fenton's reagent in an aqueous medium.

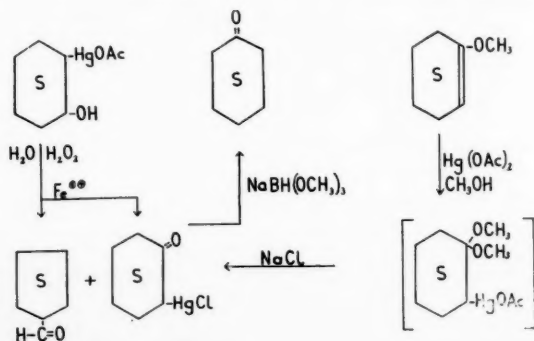
THE OXIDATION OF ORGANOMERCURIC ACETATES

More critical for a study of the oxidation are the reactions of organomercuric acetates with mercuric acetate. The rates of reaction are much slower (sometimes immeasurably so) than are the comparable reaction rates with nitrate salts. Variations which induce or accelerate reaction are more definitive for the systems containing acetate than they are for the system containing nitrate salts. However, the same type of product is obtained in either circumstance.

For example, cyclohexylmercuric acetate in methanol reacts with peracetic acid to give some (8%) mercurous acetate together with the mercuric acetate (73%) which would be expected to be formed by peracetic acid oxidation of mercurous salt. To be sure the organic product is not the expected cyclohexanol but, instead, is cyclohexanone in 75% yield. However, it would appear from the next paragraph that a secondary alcohol can be oxidized by peroxidic reagents in systems containing salts of mercury.



The participation of radicals is more apparent in the reaction of 2-hydroxycyclohexylmercuric acetate with Fenton's reagent. The expected products are mercurous salt and formylcyclopentane if the reaction proceeds like that of 2-hydroxycyclohexylmercuric nitrate with mercuric nitrate in water. Both of these products are obtained. The yields are low because of a by-product, 2-acetoxymercurycyclohexanone (isolated as its chloromercurial), which would appear to have been formed by the action of hydrogen peroxide



on the original 2-hydroxycyclohexylmercuric acetate in the system containing metallic salts. The identity of the ketomercurial, which has been reported previously (13), has been established by its reduction to cyclohexanone by means of sodium trimethoxyborohydride and by its synthesis from 1-methoxycyclohexene. Parenthetically it is of interest that sodium trimethoxyborohydride reduces the chloromercuri group preferentially with respect to the carbonyl group.

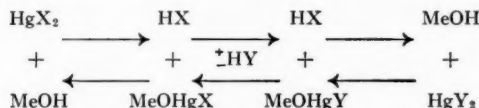
If the action of peroxy compounds on organomercuric salts leads to products like those obtained by action of mercuric salts in primary alcohols then it is reasonable to postulate that mercuric salts in alcohols are sources of radicals which act upon the organomercurials. The postulation is supported by the observation (Table II) that mercuric acetate and mercuric nitrate in methanol undergo reduction to the mercurous salts to the extent of 14% and 36% respectively at 50° in 80 to 90 hours. Since formaldehyde cannot be detected during these reductions, one may assume that the oxidation of the substrate leads to radicals which decompose to a multiplicity of simple fragments that have not been characterized.

TABLE II
The effect of acids on the reduction of mercuric salts in methanol at 50°

Expt. No.	Salt	Acid	Time (hours)	% reduction
1	0.2 M Hg(OAc) ₂	None	82	14
2	0.2 M Hg(OAc) ₂	0.2 M BF ₃ ·Et ₂ O	24	100
3	0.2 M Hg(OAc) ₂	0.2 M <i>p</i> -MeC ₆ H ₄ SO ₃ H	85	46
4	0.2 M Hg(OAc) ₂	0.2 M HNO ₃	85	42
5	0.2 M Hg(OAc) ₂	0.34 M HClO ₄	70	60
6	0.2 M Hg(NO ₃) ₂	None	88	36
7	0.2 M Hg(NO ₃) ₂	0.2 M HNO ₃	88	13

As may be seen in Table II these slow reductions are accelerated by acids, of which the most effective is boron fluoride. At first glance one might presume that the accelerations involve ionic rather than radical reactions. However, the effective participation of ionic species is doubtful in view of earlier studies of the over-all oxidation (1).

These earlier studies, involving variations in salt concentration, indicated that ionic species were not directly involved. Moreover, the effectiveness of the acid used in the over-all reaction seemed to be unrelated to its extent of dissociation insofar as acid strength in methanol are known. The same divergence may be observed in Table II. Indeed a comparison of experiments 4, 6, and 7 leads to a suspicion that the rate of reduction depends upon the extent to which a basic salt of a relatively strong acid is present. This suspicion may be expressed in terms of the following formulation of competing equilibria.



It is evident that the maximum amount of the most reactive basic salt (say MeOHgY) will be dependent upon the strengths and concentrations of HX and HY.

There ought to be kinetic significance from the evidence of Table II, and from that of Shearer and Wright (1), that the mercuric acetate - methanol system is affected by acids in the same way as is the organomercuric acetate - methanol - mercuric acetate system.

This significance is not easily apparent in the kinetically second-order reaction of organomercuric acetates with mercuric acetate in methanol because these reactions are very slow. However, as Shearer and Wright (1) showed, the oxidation is accelerated by addition of an acid like boron trifluoride to a rate that is satisfactory for kinetic study. The catalyzed reaction is kinetically first order.

Shearer and Wright specified the catalyzed reaction as first order in respect of the organomercurial and this opinion would seem to be at variance with the present evidence that the over-all oxidation is directly dependent upon the behavior of mercuric acetate in methanol. However, we have found the conclusion of Shearer and Wright to be incorrect. The over-all oxidation of organomercuric acetate by mercuric acetate in methanol containing boron trifluoride is first order with respect to mercuric acetate and not to the organomercurial.

The rate of reaction of mercuric acetate with methanol is negligible within a reasonable time in absence of boron trifluoride. The rate becomes measurable when 20 mole% of this catalyst is added. This rate is higher when 40 mole% of boron trifluoride is included but (see Fig. 2) is not increased by further addition of catalyst. The rate of disappearance

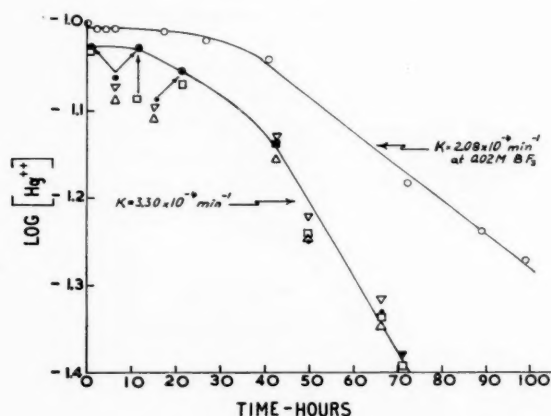
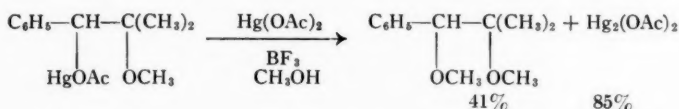


FIG. 2. Boron fluoride etherate catalysis of reduction of mercuric acetate (0.10 M) in methanol at 25° C. $[\text{BF}_3 \cdot \text{Et}_2\text{O}]$: O, 0.02 M; \square , 0.04 M; Δ , 0.06 M; \bullet , 0.08 M; ∇ , 0.10 M.

of mercuric salt with 20 mole% of catalyst is found to be identical ($k = 2.08 \times 10^{-4}$) with the rate of appearance of mercurous salt, as it was determined in a separate experiment. Moreover (see Table III), this rate is unaltered when the methoxymercurials of *trans*-stilbene (in several concentrations) and of β,β -dimethylstyrene are included.*



*The products from experiments 1-6 inclusive have been described previously. We have now found the expected phenylisobutane diether by a separate experiment which includes the reagents of experiment 7, Table III. Except for the fact that these reactions of acetate salts yield only ethers and not esters they are similar to the reaction of the analogous nitrates.

TABLE III

System: Mercuric acetate (0.10 M), boron fluoride etherate (0.02 M), and additive in methanol at 25°

Expt. No.	Additive	$k \times 10^{-4} \text{ min}^{-1}$
1	None	2.08
2	0.0025 M β -2-methoxy-1,2-diphenylethyl-mercuric acetate	1.98
3	0.050 M β -2-methoxy-1,2-diphenylethyl-mercuric acetate	1.90
4	0.050 M β -2-methoxy-1,2-diphenylethyl-mercuric acetate	2.04
5	0.075 M β -2-methoxy-1,2-diphenylethyl-mercuric acetate	2.08
6	0.100 M β -2-methoxy-1,2-diphenylethyl-mercuric acetate	2.08
7	0.050 M 2-methoxy-2-methyl-1-phenyl-propylmercuric acetate	2.03

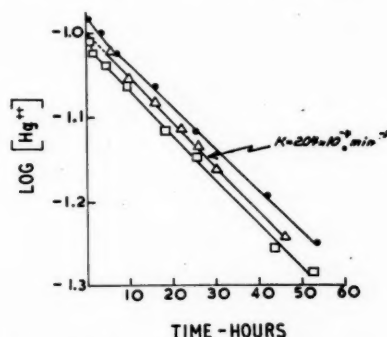
Both Table III and Fig. 3 (in which the rate, $2.04 \times 10^{-4} \text{ min}^{-1}$, of an experiment from

Fig. 3. System: Mercuric acetate (0.10 M) and boron fluoride etherate (0.02 M) in methanol at 25° C. ●, 0.05 M *trans*-stilbene (as alkene); Δ, 0.05 M *trans*-stilbene (as mercurial); □, 0.05 M β , β -dimethylstyrene (as mercurial).

reference 1 is included as the line drawn through squares) show that the reaction is first order with respect to mercuric acetate and is independent of the concentration of the organomercurial. Thus it is understandable, as is shown in Table IV, that the oxidation rates of the mercurials prepared *in situ* (1) from *cis*- and *trans*-stilbenes are practically identical. Of course these rates are greater than those shown in Table III because the boron fluoride concentration is higher relative to the molarity of mercurial.

TABLE IV

Summary of *cis*- and *trans*-stilbene oxidation rates with mercuric acetate in methanol with boron fluoride etherate added, reference 1

Molarities after mercuration				1st order
	Stilbene	Mercuric acetate	$\text{BF}_3 \cdot \text{Et}_2\text{O}$	$k \times 10^{-4} \text{ min}^{-1}$
1	<i>cis</i> 0.05*	0.05	0.02	5.68 ± 0.30
2	<i>cis</i> 0.05	0.05	0.02	5.05 ± 0.25
3	<i>trans</i> 0.05*	0.05	0.02	5.05 ± 0.30
4	<i>trans</i> 0.05	0.05	0.02	5.05 ± 0.30
5	<i>trans</i> 0.05	0.10	0.02	5.35 ± 0.30
6	<i>trans</i> 0.10	0.10	0.04	5.56

*The alkene and excess mercuric acetate were used to give the concentrations shown.

It would appear from these results that the rate-determining step in the acid-catalyzed oxidation of organomercuric acetates by mercuric acetate is the oxidation-reduction of mercuric acetate in methanol. But the over-all reaction seems to involve radicals, so one may speculate that a homopolar fission of the methoxymercuric salt is occurring



Evidence for radicals in the mercuric acetate - methanol system is afforded because an induction period occurs before mercurous salt appears. It may be seen in Fig. 4 that this induction period may be shortened markedly by removal of dissolved oxygen from the system. Of course the inhibition by oxygen also indicates that radicals are involved in the induction step.

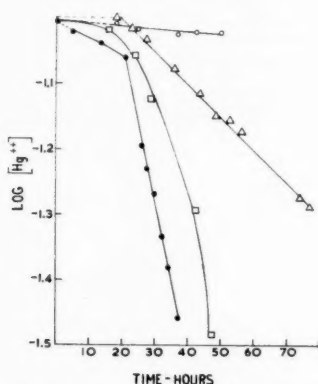


FIG. 4. System: Mercuric acetate (0.10 *M*) and boron fluoride etherate (0.02 *M*) in methanol at 25° C. O, under oxygen; Δ, under air; □, deaerated three times; ●, deaerated four times.

Since the long period of induction does not occur in the over-all oxidation, it seems probable that inducing radicals are more prevalent in the presence of an organomercuric salt than they are in its absence. This supposition is borne out by the evidence of Fig. 5.

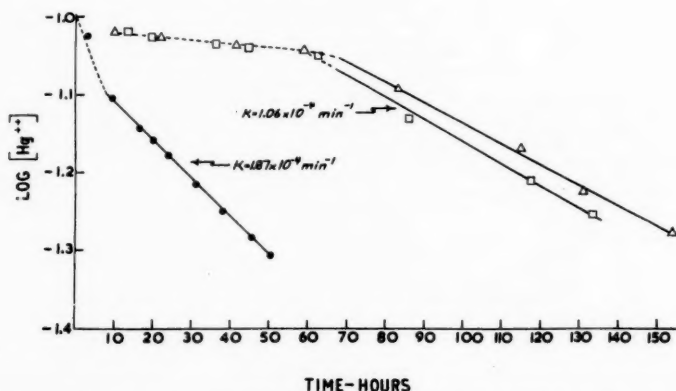
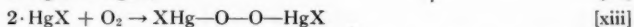
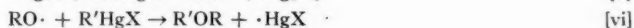


FIG. 5. System: Mercuric acetate (0.10 *M*) and boron fluoride (0.02 *M*) in methanol at 25° C. Additive: 0.05 *M* α-2-methyl-2-methoxycyclohexylmercuric acetate, ●; 0.05 *M* *n*-butylmercuric acetate, Δ; 0.05 *M* α-2-methoxycyclohexylmercuric acetate, □.

Here it is shown by the inclusion of organomercurials that *n*-butylmercuric acetate, which cannot be oxidized in the mercuric acetate - boron fluoride - methanol system, does not alter the inhibition. Neither does α -2-methoxycyclohexylmercuric acetate, the reaction of which is very slow in this system. On the other hand, the addition of 2-methyl-2-methoxycyclohexylmercuric acetate (which is oxidized rapidly in systems where the reagent concentration is stoichiometric) markedly shortens the induction period. Evidently it is acting here as a scavenger for oxygen.

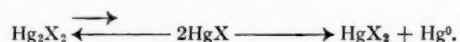
THE MECHANISM OF THE OXIDATION

In summary of the evidence which now has been presented it is suggested that for several reasons mercuric salt in methanol very slowly undergoes a homopolar fission into anionomercury radicals and a radical (acetato, nitrato, methoxy, or hydroxy) deriving from the salt or its solvolysis product in water or methanol. This behavior is expressed in equations [i], [ii], and [iii]. The radical population generated by any one of these three reactions must be so low at room temperature (especially when mercuric acetate without boron fluoride is involved) that "breeding" of a chain reaction is largely prevented by oxygen. The decomposition of some organomercuric salts into radicals, as is expressed by equation [iv], should be more extensive according to the rate at which diphenylpicrylhydrazine is bleached (Fig. 1). The elimination of inhibition by oxygen seems to be confirmatory.



These meager reactions ([i]-[iv]) cannot account for the rates at which organomercuric salts can be oxidized by mercuric salts. However, an explanation is afforded by consideration of a novel particle, anionomercury radical. If this half of a mercurous salt reacts with a basic mercuric salt according to equation [v] or with the non-solvolyzed mercuric salt by equation [vii], then stable (dimeric?) mercurous salt is formed together with a radical. This radical may be $\text{RO}\cdot$ ($\text{R} = \text{H}$ or Me) from the solvolyzed salt in water or an alcohol, say methyl alcohol, or it may be $\text{X}\cdot$ (nitrato from mercuric nitrate or else the dead radical, acetato). If the live radicals, $\text{RO}\cdot$ or $\text{NO}_2\cdot$ were to react with the organomercuric salt according to reaction [vi] or [viii], products such as alcohols, methyl ethers, or nitrate esters would be obtained together with the anionomercury radical. But this radical would then promote reactions [v] and [vii], thus establishing a self-sustaining chain. The continuation of this radical chain would therefore depend upon a supply of new anionomercury radical according to equations [i], [iii], and [iv] in order to compensate for depletion of the radical according to equations [xii] and [xiii]. Other radical-depletion reactions are suggested by equations [ix], [x], and [xi].

The anionomercuric radical which is postulated here is envisaged as an active form of monomeric mercurous salt. The idea of this monomer is not unprecedented. A low concentration in equilibrium with the dimer has been postulated on the basis of spectroscopic evidence (14), and an apparent contradiction in favor of the dismutation into mercuric ion and free mercury (15) may only show that the monomer itself is an unstable species which may dismutate.



Certainly the dismutation reaction is well known. The intermediacy of the monomer has been suggested as a boundary state in the calomel electrode (16, 17), and the position of mercury in the periodic classification of elements is appropriate for the P \rightarrow O electron shell transition which would allow of the temporal active state, $\cdot\text{HgX}$. Actually an unspecified active mercurous state has been suggested for the radical-like behaviors of the Eder reaction (18), which resembles closely the reaction that we have reported here and which we have described as a regenerative radical chain.

In our opinion the catalytic effect of acids does not conflict with our conception of a regenerative radical chain. Of course electron attraction within a group does so weaken a bond that ionic dissociation occurs. But such electrical field deformation may also equalize electron sharing in a bond, so that it becomes amenable to homopolar fission. Perhaps the best known example of this equalization influence is found in the effect of acidity upon redox potentials. Also it is significant that some of the homopolar reactions of diazotized amines are promoted by boron fluoride.

There remains the necessity to explain why the accelerating effect of boron fluoride on the organomercuric acetate - methanol - mercuric acetate system shifts the kinetic behavior from the second order observed for the uncatalyzed reaction (or for the reaction of the nitrate salts) to a first-order rate. An explanation may be offered in terms of equations [v] and [vi]. In absence of the accelerating action of boron fluoride the reaction according to equation [vi] will be rate controlling and hence will require both basic mercuric salt and organomercuric salt, each as first-order participants. But if boron fluoride catalyzes the reaction of equation [vi] (by labilization of the C—Hg bond in the organomercurial) then the anionomercuric radical will be ample for the reaction of equation [v]. In this circumstance the regenerative chain ([v] and [vi]) will depend only on the concentration of the basic mercuric salt.

One might question why the co-ordinative tendency of boron fluoride ought not also labilize the basic mercuric salt of equation [v]. If this labilization occurred to an appreciable extent the explanation presented above would not be valid. We believe it to be fortuitous that the difference in co-ordination of boron fluoride with methanolic mercuric acetate versus the organomercuric acetates that we used was sufficiently great as not to vitiate the first-order kinetics. But we would not expect to be so fortunate with other organomercuric salts. Indeed, the poor kinetic studies of the earlier report (1) may in retrospect be explained on this basis.

STEREOCHEMICAL ASPECTS OF THE OXIDATION

If this oxidation of organomercurials is indeed homopolar then the unique characteristic is its stereospecificity. Moreover, the stereospecific reaction occurs with inversion if the recent assignment of configurations for 2-methoxy-1,2-diphenylethylmercuric salts is correct (19). In terms of the Werner concept of substitution (commonly called S_N2) the stereospecific substitution via radicals may seem to be anomalous in the sense that nucleophilic attraction is absent in the neutral radical.

Of course the original Werner concept of concise co-ordination as an intermediate state of substitution by inversion has now largely been superseded by the idea of a dynamic transition. In the latter view the assignment of electrical polarity is much less significant than is required by co-ordination, even if it is ephemeral. Indeed a transition state for equation [vi] in which radicals are involved may be described as a concerted coupling and decoupling of spin, exemplified in Fig. 6.

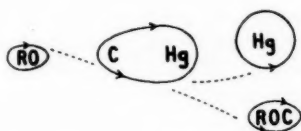


FIG. 6.

Of course it is surprising that the necessity for specification of this mechanism has not arisen previously among examples of Walden inversion. Perhaps the complexity of the usual radical reaction has disguised any stereospecificity. Indeed, the mechanism (Fig. 6) which we have proposed may turn out to be exemplified among the stereospecific polymerizations which are radical-induced and propagated.

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EXPERIMENTAL*

Reagents and Equipment

Mercuric acetate was purified by crystallization from dilute acetic acid. Mercuric nitrate (Merck reagent) was used as such; analysis showed that it contained 105.56% (gravimetric) and 104.94% (volumetric) of mercuric ion assuming anhydrous mercuric nitrate. Thus it was actually a basic salt. Absolute nitric acid (better than 99%) was distilled, water-white. Dry methanol (from magnesium methoxide) contained less than 0.002% water (Karl Fischer titration). Spectra were determined with Beckman DK-1, IR-4, and IR-5 instruments. Kinetic studies at 25° were controlled to $\pm 0.1^\circ$.

The Reduction of Mercuric Acetate in Methanol with Boron Fluoride Etherate

(a) Kinetics

The rate of disappearance of mercuric acetate was determined by volumetric analysis for mercuric salt using the method of titration with potassium iodide and mercuric nitrate. This was necessitated by the fact that mercurous salts were not completely removed as the acetate when appreciable amounts of boron fluoride were present in the methanol solutions and would have interfered with analysis by thiocyanate titration. The rate data are plotted in Fig. 2, from which the first-order rate constants were calculated. The experiment involving 1 mole equivalent of boron fluoride is given as representative.

Mercuric acetate (3.1876 g, 0.01 mole) was dissolved in 75 ml of dry methanol, and 1.260 ml (0.01 mole) of freshly distilled boron fluoride etherate added. The volume was made up to 100.00 ml and the sample thermostatted at $25 \pm 0.1^\circ$. Aliquots (4.00 ml) were added to 10 ml of 2 M hydrochloric acid and filtered through Celite to remove mercurous chloride. The filtrate and washings were diluted to 70 ml with water, 10.00 ml of 0.2 M

*Melting points have been corrected against reliable standards. X-Ray diffraction patterns are reported using $\text{Cu}(K_\alpha)$ Ni-filtered radiation in Angstroms at relative intensities $[I/I_1]$.

standard potassium iodide solution added, and then titrated with mercuric nitrate solution. The latter, used as the primary standard, was freshly prepared each 24 hours by dissolving 5.4152 g of mercuric oxide in 6.3 ml of concentrated nitric acid and diluting to 500 ml.

The rate of this reaction, using 0.02 *M* boron fluoride, was checked by analyzing gravimetrically for mercurous salt. A series of solutions containing 0.7950 g (0.0025 mole) of mercuric acetate and 0.070 g (0.0005 mole) of boron fluoride was made up to 25.00 ml in methanol and held at 25°. Periodically samples were rinsed out of the volumetric flasks with 25 ml of water containing 2 ml of 8 *M* nitric acid and then 2.0 ml of 5 *M* sodium chloride added. The mercurous chloride was recovered by filtration, using about 0.5 g of previously dried and accurately weighed Celite to facilitate the operation. The filtrate was made basic and mercuric oxide separated in the same manner. The precipitates were dried 4 hours at 50°/1 mm, giving the following data.

TABLE V
Gravimetric rate data

Time (hours)	Wt. Hg ₂ Cl ₂ (g)	Wt. HgO (g)	Total [Hg] (M)
0	0.0000	0.5402	0.0998
11.50	0.0078	0.5365	0.1002
33.50	0.0461	0.4989	0.0998
41.25	0.0548	0.4893	0.0995
57.25	0.1320	0.4195	0.0999
67.25	0.2062	0.3348	0.0969
81.75	0.2744	0.2764	0.0976
129.75	0.3925	0.1598	0.0960

When this data was plotted similarly to that shown in Fig. 2, the rates, based on the mercurous and mercuric determinations respectively, were $2.08 \times 10^{-4} \text{ min}^{-1}$ and $2.14 \times 10^{-4} \text{ min}^{-1}$.

Kinetics of the Oxidation of trans-Stilbene and its Methoxymercurial with Mercuric Acetate and Boron Fluoride Etherate in Methanol

(a) *Initially Alkene*

A suspension of 0.450 g (0.0025 mole) of *trans*-stilbene and 2.3902 g (0.0075 mole) of mercuric acetate in 40 cc of dry methanol was shaken 1 hour, causing nearly complete solution of the solids. Boron fluoride etherate (0.126 ml, 0.001 mole) was added and the volume made up to 50.00 ml, whereupon a brief shaking caused complete solution. This was then thermostatted at 25°, zero time being taken as that of boron fluoride addition.

(b) *Initially Mercurial*

Quantities of 2.235 g (0.005 mole) of β -2-methoxy-1,2-diphenylethylmercuric chloride (20) and 0.835 g (0.005 mole) of silver acetate were shaken with 25 ml of dry methanol for 1 hour then filtered to remove 0.716 g (100%) of silver chloride. To the filtrate was added 1.593 g (0.005 mole) of mercuric acetate and 0.126 ml (0.001 mole) of boron fluoride etherate. After it was diluted to 50.00 ml, the whole was shaken a few minutes to cause complete solution and kept at 25°.

In both cases (a) and (b) the analytical procedure used was the mercuric nitrate titration described above.

The Oxidation of 1-Phenyl-2-methoxy-2-methyl-propylmercuric Acetate with Mercuric Acetate and Boron Fluoride

(a) *Kinetics*

The rate of oxidation of this mercurial was determined by the method described above

and is given in Table II. The actual rate data is plotted in Fig. 3 together with the comparable experiments with stilbenes described above.

(b) Products of the Reaction

A 10.0-g (0.025 mole) quantity of 1-phenyl-2-methoxy-2-methylpropylmercuric chloride (21) was converted to its acetato analogue with 4.17 g (0.025 mole) of silver acetate in 200 ml of dry methanol (yield of silver chloride 99%). To the acetatomercurial was added 15.9 g (0.05 mole) of mercuric acetate and 6.3 ml (0.05 mole) of boron fluoride etherate, and the solution kept at 50° for 24 hours. After it was cooled to 0° and filtered from 6.02 g of solid (presumed to be mercurous acetate and testing black with alkali), the solution was concentrated to 40 ml by distillation at 15–20° under reduced pressure, and diluted with 200 ml of water. After the addition of just sufficient 8 *M* nitric acid to dissolve all solids, the suspension was extracted with chloroform (3×50 ml). The aqueous phase gave 9.51 g of chloroform-insoluble mercurous chloride when excess sodium chloride was added. Distillation of the chloroform extract yielded 2.01 g (41%) of crude 1-phenyl-1,2-dimethoxy-2-methylpropane, b.p. 94–96°/8 mm, m.p. –4.0 to +1.5°, n_D^{20} 1.4972. Literature values for this compound (1) are b.p. 94–100°/8 mm, m.p. 8–11°, n_D^{20} 1.4980.

Inhibition of Mercuric Acetate – Methanol Reaction

The data of Fig. 3 were obtained by the analytical methods described above with solutions of 1.5935 g (0.005 mole) of mercuric acetate in 100 ml of dry methanol to which 0.126 ml of boron fluoride etherate was added at zero time in a magnetically stirred flask at 26–27°. Duration of experiment was 50 hours. The reaction under oxygen was maintained at 17–19 lb absolute pressure and a yellow turbidity was observable at termination. Deaeration experiments were conducted by flushing system and solution with nitrogen, cooling by liquid air bath to incipient solidification, evacuation at 0.1 mm until cessation of bubbling, followed by complete solidification with 10 minutes of continued evacuation. The system was then warmed to 25° and pure nitrogen was admitted, followed by boron fluoride etherate. The relative first-order rates are: under oxygen, negligible; under air, $k = 1.97 \times 10^{-4} \text{ min}^{-1}$; after four deaerations, $k = 9.28 \times 10^{-4} \text{ min}^{-1}$.

Acceleration of Mercuric Acetate – Methanol Reaction

The experiment recorded in Table IV for acceleration by nitric acid is typical. A solution containing 0.935 g (0.0029 mole) of mercuric acetate, 0.120 ml of absolute nitric acid, and 15.0 ml of dry methanol was kept at 50° for 85 hours. After the solution was cooled to 0°, sufficient 8 *M* nitric acid was added to dissolve any precipitated solid, and excess sodium chloride solution (5 *M*) was added to precipitate 0.289 g (42%) of mercurous chloride. When the filtrate was basified, 0.272 g (58%) of mercuric oxide was obtained. The combined recovery of mercury salts was always $100 \pm 2\%$.

The Ultraviolet Absorption Spectra of Mercury Salts in Methanol

(a) Mercuric Nitrate

A solution of mercuric nitrate ($2 \times 10^{-4} \text{ M}$) in dry methanol showed no absorption maxima above 230 $m\mu$. At shorter wave lengths total absorption occurred. Over a period of 100 hours an absorption peak appeared at 242 $m\mu$, which was shown to be due to mercurous nitrate. When 4 mole equivalents of sodium acetate were added to this solution, the peak at 242 $m\mu$ was immediately replaced by one at 236 $m\mu$ due to mercurous acetate.

When a solution of mercuric nitrate ($2 \times 10^{-4} \text{ M}$) and absolute nitric acid ($8 \times 10^{-4} \text{ M}$) was freshly prepared it showed no absorption maxima above 230 $m\mu$, but after 24 hours a peak had appeared at 290 $m\mu$, and there was no absorption at 242 $m\mu$ attributable to mercurous nitrate. The addition of 4 mole equivalents of mercurous acetate to this solu-

tion shifted the 290-m μ absorption to 275 m μ . This latter absorption region was not observed in any of the mercuric and mercurous acetate solutions.

These spectra of mercurous nitrate solutions, showing only the maxima at 242 m μ , are not changed upon addition of 2 equivalents of sodium acetate. However, when the solutions had been left standing 100 hours the appearance of absorption at 290 m μ was observed.

(b) *Mercuric Acetate*

A solution of mercuric acetate ($2 \times 10^{-4} M$) showed no maxima below 230 m μ when freshly prepared. Over a period of 9 days a peak appeared at 236 m μ , identical with that found with mercurous acetate ($2 \times 10^{-4} M$). When a similar solution containing nitric acid ($4 \times 10^{-4} M$) was aged 10 days, only the absorptions appeared due to mercurous nitrate (242 m μ) and the unidentified mercuric species (290 m μ).

The 236-m μ peak found for mercurous acetate was shifted to 242 m μ (mercurous nitrate) upon addition of 2 equivalents of nitric acid.

Oxidation of Cyclohexylmercuric Nitrate with Mercuric Nitrate

(a) *In Methanol*

A 10.00-g (0.0313 mole) quantity of the chloromercurial was converted to the nitrate analogue with silver nitrate in 450 ml of methanol. To this solution was added 10.18 g (0.0313 mole) of mercuric nitrate and 1.32 ml (0.0313 mole) of absolute nitric acid. After 38 hours, the solution was cooled to 0°, diluted with 400 ml of water, and 15 ml of 5 *M* sodium chloride added. Filtration gave 12.79 g (87%) of chloroform-insoluble mercurous chloride. The filtrate was extracted with ether (6 \times 75 ml) which was washed with dilute base, water, dried, and distilled, giving a fraction, b.p. 25–41°/2–3 mm, n_D^{20} 1.4522, wt. 1.06 g. This material gave a positive nitrate ester test with benzidine (22) and a negative test for carbonyl compounds. A chromatoplate analysis was made on silicic acid, eluting with commercial hexane; comparison with pure compounds showed that methoxycyclohexane and cyclohexyl nitrate were present. When these pure compounds and the product mixture were submitted for infrared spectral analysis (courtesy of Canadian Armaments Research and Development Establishment, Quebec) the mixture was found to represent yields of 31% of cyclohexyl nitrate and 8% of methyl cyclohexyl ether.

(b) *In Water*

A 20.00-g (0.0627 mole) quantity of the chloromercurial and 10.65 g (0.0627 mole) of silver nitrate in 500 ml of dry methanol were stirred 1 hour, filtered from 8.98 g (100%) of silver chloride, and the filtrate taken to dryness as rapidly as possible at 20–25°. The grey residue was dissolved in 100 ml of chloroform, filtered from 0.58 g of grey solid, and again concentrated at reduced pressure to give 20.00 g (0.058 mole) of white crystals presumed to be the nitratomercurial. To this was added 140 ml of water, 18.82 g (0.058 mole) of mercuric nitrate, and 7.5 ml of 8 *M* nitric acid (0.060 mole). After it was stirred 16 hours the mixture was extracted with ether (6 \times 50 ml), and 2.51 g (0.0125 mole) of metallic mercury separated from the aqueous phase. Addition of excess sodium chloride to the aqueous phase gave 24.5 g (0.103 mole) of mercurous chloride, which was totally insoluble in chloroform.

The ether extracts, washed with dilute sodium hydroxide which produced some mercuric oxide, then with water till neutral, were dried and distilled to give two fractions: (1) b.p. 15–40°/37 mm, wt. 0.38 g; and (2) b.p. 65–84°/42–3 mm, wt. 4.14 g. The infrared spectra of both fractions were nearly identical and indicated them to be mainly a mixture of cyclohexanol and cyclohexyl nitrate. Fraction 2 was analyzed by this means, using the

hydroxyl band at 3450 cm^{-1} ($\epsilon = 98.1$) for the alcohol and the strong covalent nitrate band at 1650 cm^{-1} ($\epsilon = 1090$) for the ester. Each of these bands is free from contribution of the other component. Solution spectra in cyclohexane were used at concentrations of about 0.1 g/ml for the alcohol and 0.015 g/ml for the ester. Fraction 2 was thus found to be 43% by weight of ester and 55% alcohol. Hence fractions 1 and 2 represent yields of 40% and 21% respectively of cyclohexanol and cyclohexyl nitrate. The following principal absorption bands (cm^{-1}) were observed. Cyclohexanol: 3450, 2910, 1458, 1375, 1338, 1290, 1239, 1145, 1095, 1052, 1011, 991, 952, 930. Cyclohexyl nitrate: 3050, 2900, 1650, 1465, 1325, 1283, 1240, 993, 941, 915, 862.

A portion of fraction 2 (0.10 g) was treated with dinitrophenylhydrazine reagent to give 12 mg of the hydrazone of formylcyclopentane, m.p. $149\text{--}152^\circ$, which melting point was raised by mixture with an authentic sample.

Another portion of fraction 2 (1.92 g) was reduced with zinc and iron in acetic acid by the method of Dewar and Fort (23) to give 1.17 g of only one fraction, b.p. $158\text{--}160^\circ$, m.p. $16\text{--}22^\circ$. A test with diphenylamine was negative for nitrate ester. When this cyclohexanol (0.57 g , 0.0057 mole) was treated with 1.2 g (0.0057 mole) of α -naphthylisocyanate, there was obtained 1.53 g (100% crude yield) of urethane, m.p. $126\text{--}130^\circ$; this melting point was raised upon admixture with authentic urethane of m.p. $130\text{--}131^\circ$.

Under otherwise comparable conditions (except that the system was homogeneous) replacement of the mercurial by cyclohexanol did not lead to any cyclohexyl nitrate.

Oxidation of Benzylmercuric Nitrate with Mercuric Nitrate in Water

Benzylmercuric chloride (10.00 g , 0.0306 mole) was converted to the nitrate salt with silver nitrate in 90 ml of methanol. After filtration of silver chloride (100%), the filtrate was rapidly concentrated at reduced pressure to dryness. To this was added a clear solution prepared from 60 ml of water, 6.63 g (0.0306 mole) of mercuric oxide, and 11.15 ml (0.0918 mole) of 8.2 M nitric acid. After the solution was stirred for 10 hours, the reaction mixture was extracted with ether ($5 \times 25\text{ ml}$). Then excess sodium chloride (5 M) was added to the aqueous phase to precipitate 11.63 g (81%) of mercurous chloride, which tested black with alkali and was chloroform-insoluble. The ethereal extracts were water-washed until neutral, dried, and concentrated to 2.46 g of yellow oil. Now, 1.000 g of this oil was chromatographed on a $10 \times 250\text{-mm}$ column, using a 2:1 silicic acid: Celite adsorbent which had been activated at 150° . Two main fractions were obtained, one of which, wt. 0.360 g , tested positively for both a carbonyl and a nitrate ester (diphenylamine test) component. The second fraction contained no nitrate ester. The first fraction was dissolved in 15.0 ml of dry ethanol, and then 1.43 ml (0.025 mole) of glacial acetic acid and 0.59 g (0.0034 mole) of Girard's P reagent was added. After standing 15 hours the solution was poured into 50 ml of cold water containing 1.19 g (0.0112 mole) of sodium carbonate and was extracted in the cold with chloroform ($4 \times 20\text{ ml}$). These extracts were washed with water, dried over magnesium sulphate, and concentrated to give 0.288 g of benzyl nitrate, m.p. -23 to -17.5° , $n_D^{20} 1.5192$. A mixed melting point with authentic benzyl nitrate (m.p. -17 to -15° , $n_D^{20} 1.5205$) was raised to -19 to -16° . The yield of benzyl nitrate was 15%.

In an identical experiment the oil obtained by ether extraction was distilled, taking a 2.36-g fraction, b.p. $65\text{--}100^\circ$ (mostly boiling at $90\text{--}100^\circ$) at 30 mm . Treatment of 0.47 g of this oil with phenylisocyanate gave 0.39 g of the phenylurethane of benzyl alcohol, m.p. $76\text{--}78^\circ$ (lit. value, m.p. 78° (24)). This indicates a 16% yield of the alcohol. From the oil there was also obtained a trace amount of benzaldehyde, separated as its dinitro-

phenylhydrazone, and identified by mixture melting point. Upon standing 2 days the oil also deposited about 20 mg of benzoic acid crystals, also identified by mixture melting point.

Reactions of Mercuric Nitrate with Radical Sources

(a) With Hydrogen Peroxide

When 0.01 mole each of mercuric nitrate and hydrogen peroxide (Becco 90%) were added to 40 ml of dry methanol a test showed no formation of mercurous salt (test with sodium chloride) after 4 hours, but the addition of 3–4 mg of ferrous sulphate heptahydrate initiated an exothermic reaction. After the solution was stirred for 20 hours, 7 ml of 8 *M* nitric acid was added to give complete solution and mercurous chloride and mercuric oxide were recovered using sodium chloride and sodium hydroxide respectively, in 60% and 40% yield. When the above was repeated using 0.10 g of ferrous salt, a nearly explosive reaction resulted. However, the same amounts of reagents, in water instead of methanol, using 5 mg of ferrous salt, produced no mercurous salt after 10 hours. It was shown that mercurous nitrate in methanol was unchanged by hydrogen peroxide and ferrous salt.

(b) With Isobutyryl Peroxide in Methanol

A 0.83-mmole quantity of mercuric nitrate in 5.0 ml of dry methanol was stirred for 12 hours with 5.0 ml of an 0.17 *M* solution of isobutyryl peroxide (25) in methanol. This system was analyzed by the method of Price (26). A test for peroxide was now negative. Addition of water, sufficient nitric acid to dissolve solids, and excess sodium chloride gave 0.12 g (62%) of mercurous chloride. Addition of excess base now gave no mercuric oxide.

Reactions of Mercury Acetates with Radical Sources

No mercurous salt was formed when 0.01 mole each of mercuric acetate and hydrogen peroxide in 40 ml of methanol was treated with 5 mg of ferrous sulphate. Indeed a 36% conversion to mercuric salt was observed when a solution of 0.005 mole of mercurous acetate and 0.01 mole of 90% hydrogen peroxide in 40 ml of methanol containing 5 mg of ferrous sulphate was stirred for 5 hours. This conversion was detected by subsequent addition of 90 ml of water and 10 ml of 5 *M* aqueous sodium chloride, then sufficient 8 *M* nitric acid to just dissolve the orange-colored solid. After filtration of 1.76 g (64%) of mercurous salt the filtrate was basified to yield 0.77 g of mercuric oxide. The conversion to mercuric salt was complete when 0.05 mole of peracetic acid in 10 ml of chloroform was refluxed with 0.01 mole of mercurous acetate in 20 ml of methanol during 4 hours.

Reaction of Cyclohexylmercuric Nitrate with Pernitrous Acid in Water-Methanol

A system was prepared at 0° containing 300 ml of dry methanol, 300 ml of water, 0.06 mole of the nitrate-mercurial, 0.009 mole of 8 *M* nitric acid, and 0.09 mole of 90% hydrogen peroxide. This suspension was warmed to and maintained at 25° while a solution of 4.56 g (0.066 mole) of sodium nitrite in 60 ml of water was added dropwise during 20 minutes. Now the serial addition of the same amounts of nitric acid, hydrogen peroxide, and then (slowly and dropwise) sodium nitrite was repeated thrice, and the mixture cooled to maintain the temperature at 25°. The reaction mixture was then extracted with ether (8×50 ml), the extracts dried and distilled to give 5.51 g of oil. Treatment of a sample of this oil with dinitrophenylhydrazine gave the derivative of cyclohexanone, m.p. 150–153°, identified by mixture melting point. Infrared analysis of the oil was made by the method described above for analysis of the products of oxidation of cyclohexylmercuric nitrate with mercuric nitrate. Thus the crude product contained 32% and 39% by weight

respectively of cyclohexanol and cyclohexylnitrate. These results indicate respective yields of 30% and 25% for these products in the pernitrous acid oxidation.

The original reaction mixture, after ether extraction, was treated with excess sodium chloride solution to yield 7.41 g (52%) of chloroform-insoluble mercurous chloride (black with alkali).

Reaction of α -2-Hydroxycyclohexylmercuric Acetate and Fenton's Reagent in Water

A solution containing 0.10 mole of cyclohexene, 0.10 mole of mercuric acetate, and 200 ml of water was stirred 2 hours, at which time a test with base indicated that no mercuric salt was present. Now, over a 2-hour period, there was added, simultaneously and equivalently, 10 ml of water containing 0.10 mole of hydrogen peroxide and 0.10 mole of ferrous sulphate heptahydrate. The resulting suspension was stirred 68 hours, then extracted with ether (4 \times 50 ml). Distillation of the dried ethereal extracts gave one fraction, b.p. 90–140°, which upon redistillation yielded 1.19 g of product, b.p. 130–138°, n_D^{20} 1.4390. It was identified as formylcyclopentane (23%) via its dinitrophenylhydrazone, m.p. 153–155°, whose mixture melting point with an authentic specimen was not depressed.

To the aqueous phase was added 0.10 mole of 5 *M* sodium chloride. The precipitate, after drying, was extracted with 150 ml of hot chloroform to give 7.07 g of chloroform-soluble solid. This solid melted at 138–140° with decomposition, and could be recrystallized from acetone without change in melting point. Assuming it to be 2-chloromercuricyclohexanone, the yield was 23%. This compound has been reported by Nesmeyanov (13) to melt at 134–135°. The X-ray diffraction pattern was: [10] 6.70, 5.05, 4.99; [8] 3.49; [7] 2.99; [5] 2.36; [2] 3.78, 3.29, 3.11. Calc. for C_6H_9ClHgO : C, 21.62; Found: C, 22.1.

Oxymercuration of 1-Methoxycyclohexene

After 5 hours a system comprised of 1.12 g (0.01 mole) of 1-methoxycyclohexene (27) (n_D^{20} 1.4569, b.p. 140–141° at 750 mm), 3.18 g (0.01 mole) of mercuric acetate, and 25 ml of methanol was treated with 3.8 ml of 10% aqueous sodium hydroxide. After filtration the solvent was removed under reduced pressure. The residue was treated with 5 ml of saturated aqueous sodium chloride and alkali was added to pH 6. After 1 day the precipitated oil had solidified, 2.64 g, m.p. 99–102°. This crude material was dissolved in chloroform and diethyl ether was added. Further purification (difficult because decomposition occurred slowly with deposition of calomel) was effected by solution in dioxane and reprecipitation by addition of water, 0.25 g, m.p. 128–129.5° (with decomp.). Although the sample is impure its X-ray diffraction pattern shows identity with 2-chloromercuricyclohexanone.

Although cyclohexanone in dilute alkali is reduced to cyclohexanol by sodium trimethoxyborohydride it was possible to convert chloromercuricyclohexanone (m.p. 134–135°) to cyclohexanone, b.p. 150–160° (760 mm), n_D^{20} 1.4477, in 53% yield. A solution of 1.66 g (0.005 mole) of the mercurial in 1 ml of 6 *M* alkali at 0° was treated with 0.64 g (0.005 mole) of sodium trimethoxyborohydride during 1 hour. Distillation of the ether extract yielded 0.26 g which was converted to the 2,4-dinitrophenylhydrazone, m.p. 156–158°, not depressed by admixture with an authentic sample.

Kinetics of the Reaction of Diphenylpicrylhydrazyl (DPPH) with Nitratomercurials in Methanol

The first-order rates listed in Table I were obtained from plots of log [DPPH] versus time, an example of which is shown in Fig. 1. The reaction of DPPH and cyclohexylmercuric nitrate is given here as an example of the method.

A quantity of 1.595 g (0.005 mole) of cyclohexylmercuric chloride (freshly recrystallized, m.p. 162–163° decomp.) and 0.850 g (0.005 mole) of silver nitrate in 40 ml of methanol was shaken for 30 minutes, then filtered to remove silver chloride (0.714 g, 100%). The filtrate was added to a freshly prepared solution of 16.0 mg of DPPH in 400 ml of methanol and the whole made up to 500 ml. The per cent transmittance at 510 $m\mu$ was then measured at appropriate time intervals, using a new sample of the stock reaction solution for each measurement. The molecular extinction coefficient mentioned above ($\epsilon = 10,220$) was determined for a solution of DPPH (32.0 mg/l.) and used for calculation of the DPPH concentration. The spectrum of the solution in which the absorption maxima of DPPH had completely decayed was identical with that of a solution of diphenylpicrylhydrazine in the 440- to 800- $m\mu$ region.

Kinetics of the Oxidation of Nitratomercurials with Mercuric Nitrate in Methanol

The second-order rate constants (calculated on the basis of the rate of loss of mercuric nitrate) are presented in Table I. In each case the nitratomercurial was used. To exemplify the procedure, the experiment with cyclohexylmercuric nitrate is described.

A quantity of 0.998 g (0.00313 mole) of cyclohexylmercuric chloride was converted in the usual manner to its nitrate analogue in 25 ml of dry methanol. (If any additive was to be present, it was dissolved in this solution at this point.) The nitratomercurial solution was then added to 1.016 g (0.00313 mole) of mercuric nitrate in 10 ml of dry methanol which had been shaken for 10 minutes previously to disintegrate the lumps. Upon adding 0.260 ml (0.00626 mole) of absolute nitric acid the solution became homogeneous and was immediately diluted to 50.00 ml with dry methanol. From this there were removed 5.00-ml samples which were placed in tared centrifuge tubes. These rubber-stoppered samples were thermostatted at 25° and analyzed as follows.

Four milliliters of 2 *M* hydrochloric acid was added, the sample allowed to stand 10 minutes with occasional stirring to allow complete deoxymercuration of any oxymercurial present, then centrifuged. The precipitate was then thoroughly washed successively with 5-ml portions of water, methanol, and twice with chloroform. A slender glass rod (3 mm diameter) was found to be satisfactory for stirring in these operations and was easily rinsed free of particles with methanol. When solid particles tended to remain at the liquid-air interface, they were readily centrifuged down by first floating a layer of methanol or ether on the top. The sample was dried at 110°, then finally at 56°/1 mm, and weighed as mercurous chloride.

The rate data was plotted as the reciprocal of $[Hg^{++}]$, the latter referring to the mercuric nitrate concentration. Values for $[Hg^{++}]$ were calculated from the relationship

$$[Hg^{++}] = 0.0625 - [Hg_2Cl_2],$$

it being assumed that for each equivalent of mercuric nitrate which had reacted 1 equivalent of dimeric Hg_2Cl_2 was formed.

Formation of Polyacrylonitrile in the Oxidation System: Acrylonitrile - Cyclohexene - Mercuric Nitrate - Nitric Acid - Water

(a) In Air

A solution of 2.71 g (0.0125 mole) of mercuric oxide, 3.14 ml of concentrated nitric acid (0.050 mole), and 23 ml of water was prepared. To this was added 0.51 g (0.00625 mole) of cyclohexene and the mixture shaken 5 minutes to dissolve the alkene, whereupon 0.66 g (0.0125 mole) of freshly distilled acrylonitrile was added. After 40 minutes the solution became turbid and at 60 minutes the suspended material coagulated upon swirling. After

3 hours there was filtered 0.026 g (4% of monomer) of solid. This material gave a diffuse X-ray pattern having no diffraction lines. A sample was decomposed in hot concentrated nitric acid and then the solution made basic; there was no precipitate, indicating that the material contained no mercury.

(b) *Deaerated*

The above procedure was repeated except that the solution of mercuric nitrate, nitric acid, and water was deaerated three times prior to addition of the other reagents. After 3 hours the yield of insoluble polymer was 7%, which material had a similarly diffuse X-ray pattern.

(c) *With Methylene-bis-acrylamide Added*

This reaction was repeated a third time as outlined in the first procedure, adding 0.10 g (0.65 mmole) of methylene-bis-acrylamide. Within 5 minutes the solution had become opaque and after 3 hours it had set to a gel. Centrifugation gave 0.176 g (24% yield based on total available monomer) of solid which did not contain mercury (demonstrated by decomposition with a sulphuric - nitric acid mixture). The product gave a diffuse X-ray pattern.

Polyacrylonitrile

To a solution of 0.65 ml (0.01 mole) of acrylonitrile in 20 ml of water was added 0.10 ml of 90% hydrogen peroxide and 1-2 mg of ferrous sulphate heptahydrate. After 1 hour there was no visible change so 2 ml of 8 M nitric acid was added. The solution rapidly became turbid and after 12 hours, filtration gave 0.28 g (43%) of polyacrylonitrile. This polymer corresponded to those produced as is described above, in that it was insoluble in most common solvents, had no melting point but charred above 300°, and gave no distinct X-ray diffraction pattern after 8 hours' exposure.

Attempted Polymerization of Acrylonitrile in the Presence of 2-Hydroxycyclohexylmercuric Nitrate

A solution was prepared of 1.352 g (0.00625 mole) of mercuric oxide, 1.57 ml of concentrated nitric acid, and 23 ml of water. Cyclohexene (0.63 ml, 0.00625 mole) was added and the whole shaken for 30 minutes, at which time the homogeneous solution gave a negative test with base for mercuric ion. To this was added 0.81 ml (0.0125 mole) of acrylonitrile. A faint opalescence slowly developed, but after 1 day this had not increased to a degree which allowed separation of a solid phase.

Cyclohexylmercuric Acetate and Peracetic Acid in Methanol

A solution of 0.05 mole of peracetic acid in chloroform was added to 0.01 mole of cyclohexylmercuric acetate in 20 ml of dry methanol. After 7 hours of reflux a peroxide test was negative. The mercurous acetate was filtered off and was converted by treatment with sodium chloride to 0.20 g (8%) of calomel. The filtrate was diluted to 80 ml with water and was 4 times extracted with a total of 80 ml of chloroform. The aqueous phase yielded 1.58 g (73%) of mercuric oxide when it was treated with alkali. The chloroform phase was distilled to yield only the solvent and then 0.74 g (75%) of cyclohexanone, b.p. 150-55°, n_D^{20} 1.4497, which was characterized as the 2,4-dinitrophenylhydrazone m.p. 154-5°, mixture m.p. not depressed.

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THE AUTOOXIDATION OF ORGANOMERCURIC SALTS¹

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ABSTRACT

It has been found that besides the homopolar bimolecular oxidation of alkylmercuric salts which has been reported previously an alternative unimolecular reaction of heteropolar character may occur. The product of this heteropolar reaction is the alkene, but it probably proceeds through an alkylmercury cation since reaction in benzene leads to the Friedel-Crafts type of product. Like the homopolar reaction, the heteropolar reaction is accelerated by electron withdrawal of the anionic part of the salt. Indeed, it is believed that both mechanisms are operative among many of the mercuric salt oxidations of alkenes which previously have been reported.

The oxidation of organomercuric salts by means of mercuric nitrate and mercuric acetate plus boron fluoride (1) has recently been re-examined (2). This reaction is now believed to involve a self-sustaining radical chain in which anionomercury radical (monomeric mercurous salt) is the chain carrier. The expectation that such a reaction would be inhibited by oxygen is in fact realized. This inhibition is exemplified by an induction period which occurs especially when the system comprised of mercuric acetate and boron fluoride in methanol is used as the oxidizing medium. It is evident that if there were an oxidation reaction of different mechanism, which was not inhibited by oxygen, then this latter alternative reaction would occur preferentially. Although the alternative is not observed when the mercurial to be oxidized is sufficiently reactive (as is the case with many oxymercurials), it has been observed with simple alkylmercurials.

The reaction under present consideration differs from the homopolar reaction (1, 2) in several respects. First, it does not require an inorganic mercuric salt and therefore may be classed as an autooxidation of an alkylmercuric salt. Secondly, mercury rather than mercurous salt seems to be one product while the other is the alkene to be expected if the elements of hydrogenmercuric salt were to be eliminated from the mercurial. The reaction is not entirely a general one (we have been unable yet to oxidize a primary alkylmercuric salt), but the secondary and, especially, the tertiary mercurials are oxidized with relative ease.

Typical is the reaction of cyclohexylmercuric acetate with boron trifluoride in methanol. After 90 hours at 25° the system yields 90% of the mercury as the metal. After removal

TABLE I

Autooxidation of cyclohexylmercuric salts (0.10 mole) to cyclohexene (isolated by subsequent conversion to 2-methoxycyclohexylmercuric chloride) at 50° with catalysts (0.04 mole) in several media

Salt	Catalyst	Time (hours)	Medium	Yields, %		
				C ₆ H ₁₀	Hg ⁰	Recovered salt
OAc	None	24	Methanol	0	0	96
OAc	BF ₃ Et ₂ O	21	Methanol	88	90	0
OAc	Same	15	Benzene	73	87	0
OAc	Same	160	2,5-Dioxahexane	73	71	21
OAc	CF ₃ COOH	70	Methanol	72	92	0
CF ₃ COO	None	22	Same	79	90	0
Cl	HCl	168	Same	0	0	100
NO ₂	None	24	Same	73	97	0

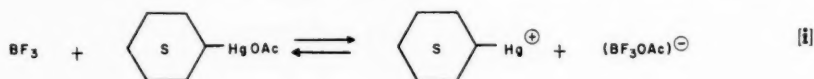
¹Manuscript received July 15, 1959.

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario.

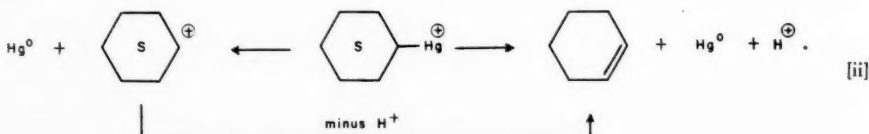
of this metal, the presence of cyclohexene in 89% yield may be demonstrated by its conversion to α -2-methoxycyclohexylmercuric chloride when mercuric acetate is added.

Although the autooxidation of the secondary alkylmercuric salt described above does not occur in absence of boron fluoride (expt. 1, Table I) it may be seen from this table that the Lewis acid must function only by increasing the polarity of the cyclohexylmercuric acetate. Thus the trifluoroacetate and the nitrate undergo the reaction without any boron fluoride. The reaction of the nitrate is especially notable because this salt reacts readily in the presence of an equivalent of mercuric nitrate in methanol by the homopolar path (2) to yield cyclohexyl nitrate and methoxycyclohexane. Contrariwise, the chloride does not undergo reaction, as might be expected in view of the stability of organomercuric chlorides.

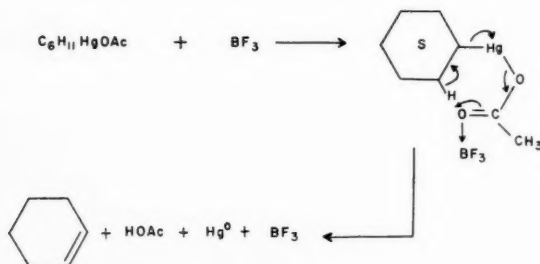
The autooxidation reactions of Table I might be described in terms of an ionization



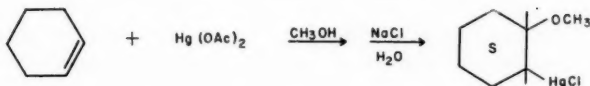
in which the cation is unstable and decomposes according to the following alternative modes



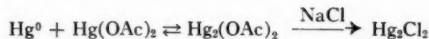
However it is probably significant that neither phenylmercuric acetate nor *n*-butylmercuric acetate in methanol precipitate metallic mercury in presence of boron fluoride. It is possible that a stereomechanism such as is shown below is operative rather than reaction via free ions.



It might be expected, if mercuric acetate were added to the cyclohexylmercuric acetate system in methanol, that the homopolar reaction would occur to give methoxycyclohexane and mercurous acetate as the products. When 2 equivalents of mercuric acetate are included the organic product is α -2-methoxycyclohexylmercuric acetate, indicating that cyclohexene is the initial product. Thus initial excess of mercuric salt does not appreciably diminish the catalytic effect of boron fluoride.



To be sure, the other product is not elemental mercury but, rather, mercurous salt. However this is not surprising because the metal ought to react rapidly with mercuric acetate according to the known dismutation (3, 4).



The maintenance of the heteropolar reaction under the conditions of the homopolar reaction may be explained in two ways. First, cyclohexylmercuric acetate, unlike the analogous nitrate salt, is not sufficiently reactive toward radicals. Secondly, the heteropolar reaction is not inhibited by oxygen. Therefore no induction period is involved such as is found in systems of mercuric acetate and unreactive organomercuric salts when the homopolar reaction occurs. This lack of an induction period is seen in Fig. 1 where the

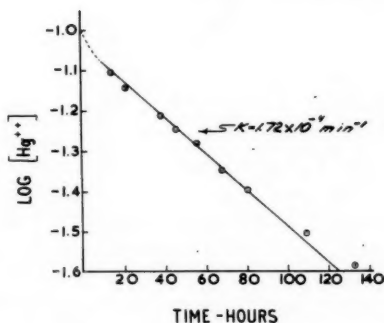


FIG. 1. System: mercuric acetate (0.10 m), cyclohexylmercuric acetate (0.05 m), and boron fluoride etherate (0.02 m) in methanol at 25° C.

actual concentration of mercuric acetate at a certain time is defined as the difference between twice the experimentally determined value and the initial value.

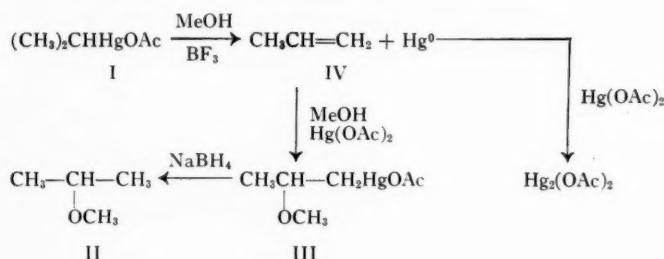
$$[\text{Hg}(\text{OAc})_2]_t = 2[\text{Hg}^{++}\text{obs.}] - [\text{Hg}(\text{OAc})_2]_0$$

This calculation is valid because the oxymercurial formed *in situ* is decomposed prior to titration.

Inspection of Fig. 1 shows that the experimental data do not justify the first order slope that is drawn through part of the points. An attempt to fit the data to second order kinetics has been equally unsatisfactory. These discrepancies are not unexpected since the yield of α -2-methoxycyclohexylmercuric salt is only 75% while the yield of mercurous salt is 105%. Indeed it would be expected that upon the termination of its induction period the reaction of mercuric acetate plus boron fluoride in methanol (2) would commence to form mercurous salt and radicals. If a reactive organomercurial were present the homopolar reaction would then proceed concomitantly with the heteropolar reaction. This duality does not occur with the unreactive cyclohexylmercuric acetate but an example will be seen later in this report.

Of course it might be postulated that the oxidation of organomercuric salts proceeds by three rather than two mechanisms. It has been assumed that free alkene is formed and then oxymercured when mercuric acetate is included in the organomercuric acetate-boron fluoride-methanol system. Alternatively, a third mechanism might be postulated in which oxidation occurred at the carbon adjacent to the acetatomercuri group. In this circumstance the formation of an oxymercurial would not be presumptive for initial formation of an alkene.

This alternative is not valid according to the reaction of 2-propylmercuric acetate (I) with boron fluoride and 2 equivalents of mercuric acetate in methanol. The product has been shown (by its reduction using sodium trimethoxyborohydride to 2-methoxypropane, II) to be 2-methoxy-1-propylmercuric salt (III) rather than 1-methoxy-2-propylmercuric salt, which would be the product of oxidation of 2-propylmercuric salt at the neighboring carbon atom. The over-all reaction may be formulated as follows.



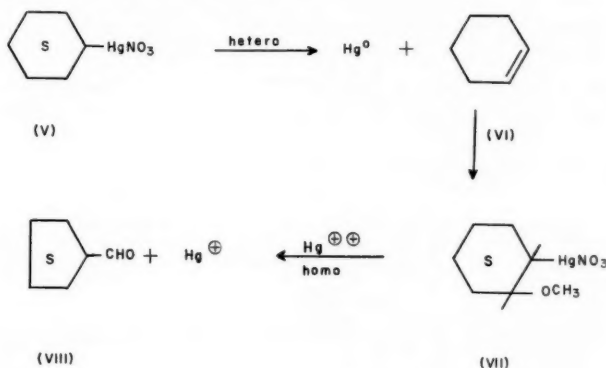
Therefore it would seem that the recognizable product from this type of oxidation derives from the alkene such as IV rather than by a third mechanism involving α -oxidation of the alkylmercuric salt.

The actual experiment, which was not terminated until all of the 2 equivalents of mercuric acetate had been consumed, does not conform stoichiometrically with the formulation outlined above. The yield of mercurous salt is 130% of that expected by this formulation, while the yield of 2-methoxypropylmercuric chloride is only 32%. A similar discrepancy has been observed in the less-definitive oxidation of 3-pentylmercuric acetate. No definite kinetic order can be specified for these reactions. While no products other than the methoxymethylmercurials are present in sufficient quantity for isolation it is significant that none of the original alkylmercuric salt is recoverable.

These deviations from stoichiometry may be attributed to the concomitant decomposition of mercuric acetate plus boron fluoride in methanol which establishes a radical chain if a susceptible organomercuric salt is present. While 2-propylmercuric acetate does not possess this susceptibility any more than does the cyclohexyl analogue it may be expected that the products of alkene oxymercuration (and especially the oxymercurials of pentene-2) will resemble 2-methoxy-2-methyl-1-phenylpropylmercuric acetate (2) more than they do the relatively stable α -2-methoxycyclohexylmercuric salt. The homopolar side reaction therefore consumes the oxymercurial derived from the alkene which is the initial product of the heteropolar reaction. It is evident that these homopolar side reactions may be minimized by deliberate oxygen inhibition.

A typical example of simultaneous reaction involving the two mechanisms has been reported in the previous publication (2) since it involves the opposite situation—where the homopolar reaction is the major one and the heteropolar reaction is minor. A small

amount of formylcyclopentane (VIII) has been observed (2), besides the main products, cyclohexanol and its nitrate ester, when cyclohexylmercuric nitrate (V) is homolytically oxidized by mercuric nitrate. Undoubtedly this trace of aldehyde (1) is formed by a separate homopolar oxidation of 2-methoxycyclohexylmercuric nitrate (VII) which is derived *in situ* from cyclohexene (VI). This alkene will be formed by the heteropolar oxidation of V such as is reported in Table I.



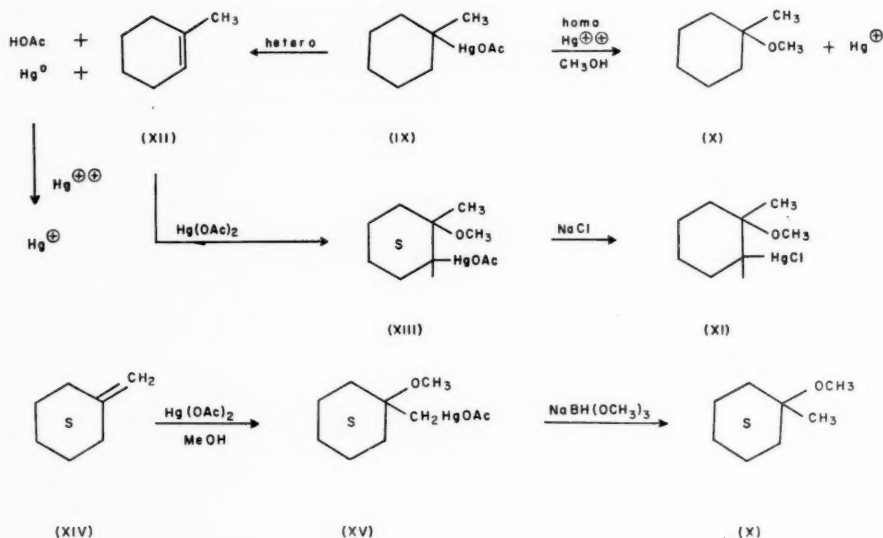
The simultaneous homopolar and heteropolar process on a single mercurial is shown also in the single instance of reaction with a tertiary alkylmercuric salt which we have been able to carry out. With this 1-methyl-1-cyclohexylmercuric salt no boron fluoride is required. Even the chloride survives only a few hours at 25° before it decomposes to metallic mercury and an oil. The acetatomercurial (IX) cannot be isolated but we have prepared it *in situ* by addition of silver acetate to a slurry of 1-methyl-1-chloromercuri-cyclohexane in a solution of mercuric acetate (2 equivalents) in methanol. It is evident from the rapidity of reaction that electron repulsion in the alkyl group precludes the necessity for electron attraction by a Lewis acid.

Three products have been isolated from a complex mixture. The isolated non-mercurial has been shown to be 1-methoxy-1-methylcyclohexane (X, estimated yield 25%) by comparison of its physical constants (5) and its R_f on a chromatoplate (6). This product is the expected one from the homolytic oxidation described in earlier reports (1, 2).

Not all of the substances containing mercury have been separated from the mixture of products, and the yields of substances which have been isolated are not significant because of the difficulties of separation. Several per cent of 2-methoxy-2-methylcyclohexylmercuric chloride (XI) has been isolated, which indicates that the heterolytic autooxidation also has been taking place via XII and XIII.

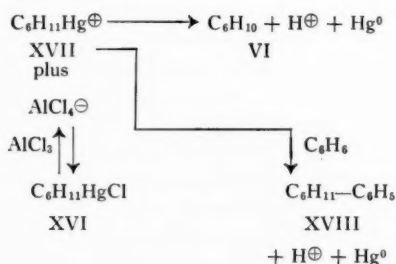
Another organomercuric salt was also isolated but it has not been identified. It is not 1-chloromercurimethyl-1-methoxycyclohexane (XV) because this substance has been synthesized for the purpose of comparison from methylenecyclohexane (XIV) (7) and its structure has been proved by reduction to 1-methoxy-1-methylcyclohexane.

This non-identity should not be construed as evidence that XV is not present in the mixture of products obtained from 1-methylchloromercuricyclohexane. It does show that the oxidation is more complex than may be shown by the formulation which is outlined above. But of prime significance is the evidence that when the C—Hg linkage is sufficiently weak the electron-withdrawing action of a Lewis acid is not required. Moreover, the



reaction shows that the lability of the C—Hg bond is specifically neither homo- nor hetero-polar, but rather is responsive to the environment in which it exists.

Nevertheless, the effect of the electron-withdrawing agent is profound. Thus it may be seen in Table I that cyclohexylmercuric chloride (XVI) is stable in methanol in presence of hydrochloric acid; also it is stable in benzene—hydrogen chloride. However the addition of 0.4 equivalent of aluminum chloride induces reaction in benzene to a 75% yield of cyclohexylbenzene (XVIII).



The reaction may proceed via the cyclohexylmercuric cation (XVII), or else cyclohexene (VI) may be an intermediate. Certainly the same product is obtained by treatment of cyclohexene in benzene with aluminum chloride. On the other hand the product is not cyclohexene but, rather, a polymer when the reaction is carried out in cyclohexane rather than benzene. Neither cyclohexene nor bicyclohexyl is detectable. In further extensions of the reaction *sec*-butylmercuric chloride yields *sec*-butylbenzene, but *n*-butylmercuric chloride does not react.

DISCUSSION

Although the heteropolar autooxidation of organomercurials has not been reported previously there are numerous papers dealing with the oxidation of alkenes by mercuric salts. In our opinion all of these oxidations involve an oxymercurial as an intermediate. Only one of these, the reaction of safrole with mercuric acetate (8, 9), may be explained as a homopolar oxidation of the intermediate. The remainder (references 10-17 inclusive) may be explained on the basis of the products in terms of heteropolar autooxidation of an intermediate oxymercurial. To be sure a concomitant homopolar oxidation cannot be precluded in these oxidations. The yield of product typical of heteropolar autooxidation is not high, so the unidentified by-products may well be the result of homopolar oxidation. Indeed it is possible that the yield of the desired products might be augmented by sufficient oxygen concentration to inhibit the homopolar reaction. In this instance a single equivalent of mercuric acetate per mole of alkene ought to be sufficient, especially if boron fluoride were added as well.

The authors acknowledge financial aid from the National Research Council of Canada, which has been used to support this investigation.

EXPERIMENTAL*

*Autooxidation of Cyclohexylmercuric Acetate**(a) In Methanol*

A solution of cyclohexylmercuric acetate (0.005 mole) was prepared by filtration of silver chloride (quantitative) after a solution of cyclohexylmercuric chloride (0.005 mole, 1.60 g) in 50 ml of methanol was treated with 0.005 mole (0.84 g) of silver acetate. The filtrate was then treated with 0.002 mole (0.25 ml) of boron fluoride etherate and was maintained at 50° for 24 hours. Then the cooled system was filtered to remove metallic mercury (0.99 g, 99%) and the filtrate was treated with 1.60 g (0.005 mole) of mercuric acetate. After 30 minutes the system, chilled to 0°, was treated with 100 ml of water and 2.5 ml of 5 *M* aqueous sodium chloride. Filtration gave 88% (1.52 g) of α -2-methoxycyclohexylmercuric chloride, m.p. 112-113°, identified by mixture melting point. When the same experiment was carried out at 25° during 72 hours the yield of mercury was 90%, and 84% of the organomercurial was obtained. Expt. 5, Table I, shows an identical experiment except that trifluoroacetic acid was used instead of boron fluoride etherate.

(b) In Methanol with 2 Equivalents of Mercuric Acetate

This reaction was followed kinetically. A solution of 0.005 mole of cyclohexylmercuric acetate in 50 ml of methanol was prepared from 1.595 g (0.005 mole) of cyclohexylmercuric chloride and 0.834 g (0.005 mole) of silver acetate. After quantitative removal of silver chloride, 0.252 ml (0.002 mole) of boron trifluoride etherate and 3.188 g (0.01 mole) of mercuric acetate were added. The solution was made up to 100 ml with methanol and was maintained at 25°. Analyses were made by removal of mercurous salt and unchanged cyclohexylmercurial by dilute hydrochloric acid according to the method described previously (2). We used 3-ml aliquots and allowed the solution before filtration to stand 30 minutes to ensure complete decomposition of the 2-methoxycyclohexylmercuric salt. The filtrate was titrated for unchanged and regenerated mercuric salt. The results are shown in Fig. 1.

*Melting points have been corrected by reference to reliable standards. X-ray patterns are reported in Å at intensities $[I/I_1]$ using Cu K_α (Ni-filtered) radiation.

A duplicate reaction system was maintained *in toto* for 37 hours at 50° and then was filtered to remove 5.48 g (105%) of mercurous acetate. The filtrate was diluted with 200 ml of water plus 10 ml of 5 *N* aqueous sodium chloride, and then was five times extracted with 25-ml portions of chloroform. Evaporation of the extracts left 2.62 g (75%) of α -2-methoxycyclohexylmercuric chloride, m.p. 113–114°, identified by mixture melting point. The absence of β diastereomer was shown by solution of 0.5 g in 8 ml of methanol to which 0.2 ml of concentrated hydrochloric acid was added. After the solution was swirled for exactly 1 minute 1 ml of 6 *M* aqueous sodium hydroxide and then 8 ml of water were added quickly. After filtration through Celite the filtrate was acidified by carbon dioxide and finally by acetic acid. There was no precipitation of β diastereomer.

(c) *In Benzene*

The solution of cyclohexylmercuric acetate (0.005 mole) in methanol was evaporated to dryness under reduced pressure and then was dissolved in 50 ml of benzene containing 0.002 mole (0.25 ml) of boron fluoride etherate. After 15 hours at 50° the system was cooled and filtered to remove 0.87 g (87%) of metallic mercury. The filtrate distilled totally, showing that no mercurial remained. The distillate was treated with 100 ml of methanol and 1.60 g (0.005 mole) of mercuric acetate. After 15 hours the system was evaporated under reduced pressure (20–25°) and the residue, dissolved in water-methanol, was treated with sodium chloride to yield 1.27 g (73%) of α -2-methoxycyclohexylmercuric chloride, m.p. 108–111°, identified by mixture melting point.

(d) *In 2,5-Dioxahexane*

In an otherwise identical system dioxahexane replaced benzene. After 160 hours at 50° the cooled system was filtered to remove 0.71 g (71%) of metallic mercury. Vacuum distillation at 20° left 15 ml which, treated with aqueous sodium chloride, yielded 0.34 g (21%) of cyclohexylmercuric chloride. The distillate, treated with 60 ml of methanol and 0.005 mole of mercuric acetate for 30 minutes, was again vacuum-evaporated. Treatment of the residue with aqueous sodium chloride yielded 1.01 g (73%) of α -2-methoxycyclohexylmercuric chloride, identified by mixture melting point.

Autooxidation of Cyclohexylmercuric Trifluoroacetate

The silver trifluoroacetate used in this experiment was prepared from silver oxide and trifluoroacetic acid (0.354 mole). After evaporation at 0.1 mm the residue was dissolved in benzene (75 ml), and 50 ml of hexane was added. The precipitate was evidently a complex with benzene since 25.2 g, finely ground, was reduced in weight to 22.2 g at 55° (0.1 mm). The X-ray diffraction pattern was: [10] 6.10, 3.60; [8] 2.33; [7] 2.58; [5] 3.00; [4] 2.70; [2] 3.31, 2.50; [1] 4.74, 3.95, 3.11. Calc. for $C_6H_{10}O_2Ag$: Ag, 48.84. Found: Ag, 48.55, 48.68.

The mercurial was prepared from 0.005 mole (1.60 g) of cyclohexylmercuric chloride and 0.005 mole (1.11 g) of silver trifluoroacetate in 50 ml of methanol; the silver chloride was filtered off. After 22 hours at 50° the system was processed as was described for the acetate-boron fluoride experiments to yield mercury (92%) and α -2-methoxycyclohexylmercuric chloride (70%).

Autooxidation of Cyclohexylmercuric Nitrate

A solution of 0.005 mole of cyclohexylmercuric chloride in 50 ml of methanol was treated with 0.005 mole (0.85 g) of silver nitrate and the silver chloride was filtered off. Subsequent processing, like the acetate, after 1 day at 50° yielded mercury (97%) and α -2-methoxycyclohexylmercuric chloride (73%).

Reaction of Organomercurials with Hydrogen Chloride

A 94% recovery of isopropylmercuric chloride was effected after 1-hour reflux with 4 ml concentrated hydrochloric acid in 15 ml of methanol; similarly with cyclohexylmercuric chloride. The same behavior was observed at 25° for 1 day with hydrogen-chloride-saturated methanol. In none of these instances was inorganic mercury detectable. On the other hand, 1 g (0.0031 mole) of benzylmercuric chloride in 15 ml of hydrogen-chloride-saturated methanol at 50° for 24 hours yielded only 0.39 g (39%) of unchanged chloromercurial (mixture melting point) upon dilution with water. The basified filtrate yielded 0.35 g (53%) of mercuric oxide.

Reaction of Phenylmercuric Acetate with Boron Fluoride

A solution of 0.005 mole of phenylmercuric acetate, 0.002 mole of boron fluoride etherate, and 50 ml of dry methanol was held at 50° for 24 hours but no metal precipitated. Subsequently 98% of the original mercurial was recovered as phenylmercuric chloride, m.p. 250–251°, mixture melting point not lowered.

Isopropylmercuric Chloride

This preparation is reported as typical for alkylmercuric halides since the procedure is simplified beyond others reported in the literature, while the yields are oftentimes better, especially for some unstable halogenomercurials.

The filtered Grignard reagent from 0.20 mole of isopropyl chloride in 120 ml of dry ether was stirred while 0.24 mole (64.8 g) of dried mercuric chloride was added in portions during 2 hours. The resulting suspension was stirred for 24 hours, more dry ether being added if necessary to ensure efficient stirring. Then 250 ml of water was added cautiously and the ether was removed while the system (below 10°) was stirred under reduced pressure. The final slurry was filtered, air-dried, and dissolved with trituration in 400 ml of chloroform at 25°. After a final brief temperature increase to 45° the solution was filtered and the filtrate was evaporated under reduced pressure leaving 47.6 g (86%) of isopropylmercuric chloride, m.p. 94.5–95.5°, not raised by recrystallization from commercial hexane or 85% aqueous methanol. Calc. for C_3H_7HgCl : C, 12.9; H, 2.53. Found: C, 13.0; H, 2.71. This product in methanol could be converted to the nitrate salt by means of silver nitrate and thence by treatment with sodium bromide to isopropylmercuric bromide, m.p. 90.5–91.5°. A mixture melting point with the chloromercurial was depressed to 77–82°.

Cyclohexylbenzene

A solution of 1.59 g (0.005 mole) of cyclohexylmercuric chloride, 0.27 g (0.002 mole) of aluminum chloride, and 50 ml of benzene was stirred for 6 hours and then was decanted from 0.77 g (77%) of metallic mercury. The solution was then washed with water until it was neutral, during which time 0.22 g (19%) of mercurous chloride separated. The non-aqueous layer was distilled up to 80° to prove that the distillate contained no cyclohexene (test with mercuric acetate and methanol) and then was distilled further, b.p. 108–110° at 12 mm, 0.66 g (75%), m.p. 4.5–6.5°. This product was identified by mixture melting point with an authentic sample prepared from cyclohexene, hydrogen chloride, aluminum chloride, and benzene (18).

When this experiment was carried out in cyclohexane rather than benzene, 92% of the mercury was precipitated as metal, but only a gummy mass with no cyclohexene or bicyclohexyl was obtained as the organic product.

sec-Butylbenzene

A slurry of 8.00 g (0.027 mole) of *sec*-butylmercuric chloride (19), 1.49 g (0.0112 mole) of aluminum chloride, and 100 ml of dry benzene was stirred for 15 hours and then decanted onto ice. The metallic mercury was separated (3.66 g, 67%). The benzene phase, washed with dilute alkali and then water, was dried (magnesium sulphate) and distilled, b.p. 170–173° (750 mm), 2.74 g (75%), n_D^{20} 1.4908 (20). When *n*-butylmercuric chloride was used instead of the secondary isomer it was recovered quantitatively.

*2-Methoxypropylmercuric Chloride**(a) From Isopropylmercuric Acetate*

A quantity of 2.79 g (0.01 mole) of isopropylmercuric chloride in 50 ml of methanol was converted to the acetate by means of silver acetate (0.01 mole). After filtration of the silver chloride, 6.38 g (0.02 mole) of mercuric acetate and 0.50 ml (0.004 mole) of boron fluoride etherate were added together with methanol to a total volume of 100 ml. After 37 hours at 50°, 6.26 g of mercurous acetate was filtered off and the chilled filtrate was diluted with 120 ml of water to which 10 ml of 5 *M* aqueous sodium chloride was then added. The resulting suspension was 5 times extracted with chloroform (125 ml total), and the aqueous phase was then filtered to remove 0.52 g of mercurous chloride (total Hg_2^{++} , 0.0132 mole or 132%). Vacuum evaporation of the chloroform left 1.00 g (32%) of yellow oil, m.p. –15° to –12.5°. Three crystallizations from methanol (2.5 ml per g) raised the melting point (–9 to –7.5°), and a mixture melting point with the authentic specimen described below was not lowered.

(b) From Propene

Propene gas was bubbled into a stirred suspension of 15.9 g (0.05 mole) of mercuric acetate in 75 ml of methanol at 0° at such a rate that a slight positive pressure was maintained in the closed system. When the pressure rose sharply and the test for mercuric ion was negative, the system was poured into 150 ml of cold water and 15 ml of 5 *M* aqueous sodium chloride was added. The oil was taken up by four extractions with a total of 120 ml of chloroform. The extract was dried (calcium chloride) and vacuum-evaporated, 15.24 g (99%), m.p. –7 to –4°. Three crystallizations from methanol (3 cc per g) left 10.4 g, m.p. –5.5 to –4.5°. After several days at –10° this substance started to decompose, yielding calomel. The organomercurial was analyzed by a micro method (21). Calc. for C_4H_9ClHgO : Hg, 64.9; Cl, 11.47. Found: Hg, 64.8; Cl, 11.63.

*2-Methoxypropane**(a) From 2-Methoxypropylmercuric Chloride*

A solution of 7.15 g (0.025 mole) of 2-methoxypropylmercuric chloride in 35 ml of water plus 5 ml of 6 *M* aqueous sodium hydroxide was chilled to 0° while 6.39 g (0.05 mole) of sodium trimethoxyborohydride was added during 1 hour. The system was then warmed to 60° to distil the ether into an ice-cold receiver. Redistillation gave 1.20 g (65%) of 2-methoxypropane, b.p. 32–33°, d_4^{25} 0.720, n_D^{20} 1.3532.

(b) From 2-Propanol

Sodium (0.16 g-atom, 3.68 g) was dissolved in 125 ml of dry 2-propanol. Then 17 g (0.12 mole) of methyl iodide was added and the solution was refluxed for 1 hour. Distillation gave 6.7 g (75%), b.p. 32–33°, d_4^{25} 0.719, n_D^{20} 1.3532. A similar preparation of 1-methoxypropane gave constants as follows: b.p. 38°, d_4^{25} 0.727, n_D^{20} 1.3584.

3-Chloromercuripentane

This substance was prepared from 3-chloropentane (22) by the general method for alkyl chloromercurials outlined above, 79% crude yield, m.p. 18–20°. Crystallization from commercial hexane (3 ml per g) raised the melting point to 21.3–21.7°. The substance was unstable and formed calomel slowly at 25°. Mercury analysis was effected by Walton's method (23). Calc. for $C_5H_{11}ClHg$: C, 19.5; H, 3.62; Hg, 65.3. Found C, 18.9; H, 3.61; Hg, 65.1.

Mixture of Vicinal Methoxypentylmercuric Chlorides

(a) From 2-Pentene

A solution of 2-pentene (b.p. 36–36.5°, n_D^{20} 1.3816) (24) and 4.47 g (0.014 mole) of mercuric acetate in 12 ml of dry methanol gave a negative test for mercuric ion within 15 minutes. The solution was poured into 24 ml of water containing 4 ml of 6 *M* aqueous alkali and the whole was filtered through Celite for clarification. To the chilled filtrate was added 3 ml of 5 *M* aqueous sodium chloride and then gaseous carbon dioxide was added until precipitation of oil was complete. The oil was collected in chloroform and the extract was evaporated leaving 3.36 g (71%) of non-crystallizable oil. The infrared spectrum (2–15 μ) showed the following absorption bands (cm^{-1}): 2950(s), 1465(m), 1382(m), 1326(m), 1196(m), 1185(m), 1152(m), 1080(s), 1028(w), 992(w), 921(w), 886(w), 832(w), 802(w), 758(w).

(b) By Autooxidation of 3-Acetatomercuripentane

A solution of 3-chloromercuripentane (3.07 g, 0.01 mole) in 30 ml of dry methanol was converted to the acetatomercurial by treatment with an equivalent of silver acetate. After removal of silver chloride (100%), 6.38 g (0.02 mole) of mercuric acetate and 0.50 ml of boron fluoride etherate were added. The system was made up to 100 ml with methanol and maintained for 44 hours at 50°. Then 5.81 g of mercurous acetate was filtered off, and the chilled filtrate was diluted with 120 ml of cold water followed by 10 ml of 5 *M* aqueous sodium chloride. Five extractions with chloroform removed the oxymmercurials leaving 0.13 g of calomel filterable from the aqueous phase (total Hg_2X_2 0.012 mole, 120%).

The crude oxychloromercurial was purified by solution in aqueous alkali followed by treatment of the filtered solution with gaseous carbon dioxide. The product, recovered by chloroform extraction, gave an infrared spectrum superimposable upon that obtained by the product of procedure (a).

1-Methylcyclohexylmercuric Chloride

Fractionally distilled 1-methyl-1-chlorocyclohexane (25) (b.p. 77.5–78.0° at 73 mm, n_D^{20} 1.5484), 0.5 g in 5 ml of dry ethyl ether was stirred with 0.73 g (0.03 g-atom) of magnesium. This metal (stored under dry ether until it was used) had previously been activated by treatment with bromobenzene from which it was subsequently freed by thorough washing by dry ether.

After the reaction had commenced (cloudiness) a solution of 3.2 g of the chloride (total 0.027 mole) in 30 ml of dry diethyl ether was added during 8 hours. After 12 hours of further stirring 7.60 g (0.028 mole) of mercuric chloride was added rapidly. The suspension was stirred for another 7 hours, then was diluted with 70 ml of chloroform and the whole was filtered. Vacuum evaporation of the filtrate left a crystalline mass which was dissolved at 25° in 25 ml of acetone. This solution at –80° precipitated 0.92 g of white needles. A second similar crystallization from acetone gave 0.79 g (9.4%) of 1-methyl-

cyclohexylmercuric chloride, no definite melting point. The X-ray diffraction pattern was [10] 9.50; [6] 4.02; [5] 3.70; [4] 4.60, 3.49; [3] 4.89, 3.29, 2.85; [2] 4.44, 4.29. Calc. for $C_7H_{13}ClHg$: C, 25.2; H, 3.93; Hg, 60.2. Found: C, 25.3; H, 3.70; Hg, 60.2, where the analysis for mercury was that of Whitmore and Sobatzki (26). The substance decomposed quickly at 25° but was stable for a few days at -70° .

1-Methylcyclohexylmercuric Acetate with Mercuric Acetate in Methanol

A slurry was prepared by dissolving 5.83 g (0.0183 mole) of mercuric acetate in 45 ml of dry methanol, then adding 1.55 g (0.0093 mole) of silver acetate and finally 3.09 g (0.0093 mole) of 1-methyl-1-chloromercuricyclohexane. The system was stirred 4 hours and then a gray solid was filtered off. This solid was shaken with 40 ml of 13% aqua ammonia to dissolve the silver chloride and leave 3.70 g (0.0178 mole) of mercurous oxide.

The methanolic filtrate at 0° was diluted with 100 ml of water, and 3 ml of 5 *M* aqueous sodium chloride was added. This diluate was extracted seven times with a total of 175 ml of ether. The extract was washed four times with a total of 120 ml of 1 *M* aqueous sodium hydroxide and then with water until the non-aqueous phase was neutral.

The combined alkaline and aqueous washing was filtered to remove 0.83 g (0.0038 mole) of mercuric oxide. The filtrate was acidified with carbon dioxide and then four times extracted with a total of 100 ml of chloroform. Vacuum evaporation of this extract left 1.52 g, m.p. $70-120^\circ$. Extraction with 3 ml of commercial hexane left an insoluble fraction which was crystallized from 3:7 water-methanol (8 ml per g), 0.57 g, m.p. $122-124^\circ$. This unidentified mercurial is base-soluble and easily demercurated by the action of methanolic hydrogen chloride. It is not 2-methoxy-2-methylcyclohexylmercuric chloride, described below.

The hexane-soluble part of the crude product extraction was evaporated and the residue was crystallized repeatedly from commercial hexane (20 ml per g), 0.06 g (3%), m.p. $79-80^\circ$, which was identified by mixture melting point with an authentic specimen (27).

The ether phase from which the alkaline phase containing the mercurials was separated was dried with magnesium sulphate and then distilled, 0.29 g, b.p. $130-140^\circ$. Redistillation gave 0.11 g (25% crude, 9% redistilled) of 1-methoxy-1-methylcyclohexane, b.p. $140-150^\circ$, n_D^{20} 1.4422. The identity with an authentic sample (b.p. $147-149^\circ$, n_D^{20} 1.4427) prepared according to Triebs' procedure (5) was established by a chromatoplate analysis in which silicic acid was the adsorbent and benzene was the eluant. The chromatogram was developed by use of a nitric-sulphuric acid spray.

1-Chloromercurimethyl-1-methoxycyclohexane

Hexahydrobenzyl acetate was pyrolyzed to methylenecyclohexane by Arnold's method (7). This alkene (0.96 g, 0.01 mole) and 3.19 g (0.01 mole) of mercuric acetate were shaken for 1 hour in 12 ml of dry methanol, then the system was chilled, diluted by 35 ml of cold water, and 3.0 cc of 5 *M* aqueous sodium chloride was added. The 3.33-g (91% crude) yield, m.p. $59-64^\circ$, was thrice crystallized from commercial hexane (8 ml per g), m.p. $68.3-69.0^\circ$. Calc. for $C_8H_{15}ClHgO$: C, 26.5; H, 4.16. Found: C, 26.6; H, 4.30.

A solution of 6.9 g (0.019 mole) of this mercurial in 4 ml of 6 *M* aqueous sodium hydroxide plus 35 ml of water was stirred at 0° while 4.85 g (0.038 mole) of sodium trimethoxyborohydride was added during 30 minutes. The ether extract of this system was then dried with magnesium sulphate and distilled, 1.73 g (71%), b.p. $145-148^\circ$, n_D^{20} 1.4414. This 1-methoxy-1-methylcyclohexane was identified by chromatoplate and also by comparison with the sample prepared by Triebs' method (5) according to the following

infrared spectra: 3120, 2700, 1425, 1334, 1308, 1265, 1245, 1180-1020, 953, 918, 875, 845, 810, 697 cm^{-1} .

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HYDROGEN BONDING IN THE AMINE HYDROHALIDES

II. THE INFRARED SPECTRUM FROM 4000 TO 2200 CM^{-1}

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ABSTRACT

The infrared spectra of a number of amine hydrohalides have been measured in the lithium fluoride region.

Hydrogen bonding and the torsional oscillations of the NH_3^+ groups influence these spectra characteristically. The $\text{N}^+-\text{H} \cdots \text{X}^-$ stretching frequencies give broad or fairly broad bands. They are near 3000 cm^{-1} for aliphatic primary amine salts. The corresponding band lies at somewhat lower frequencies for secondary amine salts and much lower for tertiary ones. The aromatic amine hydrohalides exhibit these bands at lower frequencies than do the aliphatic amine salts of the same order. There is a shift to higher frequencies in the series hydrochloride, hydrobromide, hydriodide.

All these spectra contain a number of sharper bands which may or may not coincide with the hydrogen-bonded stretching bands. These are combination bands involving mainly deformation vibrations, and they shift to lower frequencies, throughout the series hydrochloride, hydrobromide, hydriodide.

The importance of electrical anharmonicity for the appearance of these bands is stressed. The hydrogen bonds in amine hydrohalides appear to be largely electrostatic in character.

INTRODUCTION

The infrared spectra of ammonium halides were investigated by Wagner and Hornig (1, 2) and by Plumb and Hornig (3, 4). A primary aliphatic amine hydrohalide, methylamine hydrochloride, was treated by Waldron (5). Tertiary amine hydrohalides were discussed by Lord and Merrifield (6). More recently Chenon and Sandorfy (7) discussed some general aspects of the infrared spectra of amine hydrohalides measuring the spectra of a number of aliphatic and aromatic primary, secondary, and tertiary amine hydrochlorides, hydrobromides, and hydriodides. (This paper will be referred to henceforth as I.)

This series of compounds offers particular advantages for the study of hydrogen bonding. By studying the different hydrohalides of the same amine we can introduce a gradual change in hydrogen bond energy and by considering the amines of different order we can vary from one to three the number of hydrogen atoms which may be affected by hydrogen bonding. The effect of the more distant molecular environment may be studied by taking various aromatic and aliphatic amines. The effect of the net charges on the end atoms may also be examined.

In paper I, a general review of the subject was given. At present we intend to consider the high frequency part of the infrared spectrum (4000 to 2200 cm^{-1}) in more detail. This will lead us to a closer look at the nature of hydrogen bonding in these cases.

EXPERIMENTAL

A Perkin-Elmer model 112 single beam - double pass instrument was used with a lithium fluoride prism.

The whole instrument was put under a dry nitrogen atmosphere in order to eliminate atmospheric water and CO_2 absorption. All the spectra were taken in both nujol and fluorocarbon oil mulls. No significant differences were observed between the spectra taken in these two media.

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RESULTS

The spectra of the three hydrohalides of the following amines were measured.

- (a) Aliphatic primary amines: ethylamine, *n*-butylamine, *sec*-butylamine, isobutylamine, *tert*-butylamine, cyclohexylamine.
- (b) Aliphatic secondary amines: diethylamine, di-*n*-butylamine, piperidine.
- (c) Aliphatic tertiary amines: triethylamine, tri-*n*-butylamine.
- (d) Aromatic primary amines: aniline, α -naphthylamine, β -naphthylamine.
- (e) Aromatic secondary amines: diphenylamine, *N*-methylaniline.
- (f) Aromatic tertiary amines: pyridine, *N,N*-dimethylaniline, *N*-methyl diphenylamine.

Tables I and II give one typical example for each of classes (a) to (f). The data concerning the bands located between 2200 and 1900 cm^{-1} are taken from paper I (sodium chloride prism).

INTERPRETATION OF THE SPECTRA

(A) Aliphatic Primary Amine Salts

It was not possible under the low resolution of the sodium chloride prism and with a number of CH_3 and CH_2 groups present in the molecules to disentangle the coincident CH_3 , CH_2 , and NH_3^+ or NH_2^+ absorption near 3000 cm^{-1} . This remains difficult using the lithium fluoride prism. It is quite clear, however, that in the case of aliphatic primary and secondary amine salts there is a strong and fairly broad band system in partial coincidence with CH_3 and CH_2 bands. This band system must contain the two NH_2^+ or NH_3^+ stretching bands or, in the case of the latter, the three stretching bands if the symmetry is lower than C_{3v} .

The spectra of the aliphatic primary amine salts, shown in Table I, bear a great resemblance to those of the ammonium halides (1, 2, 3, 4) and seem to be quite analogous to the spectrum of methylamine hydrochloride discussed by Waldron (5), who measured this spectrum at 300° K, 90° K, and 230° K. At each of these temperatures the compound exists in a different phase designated α , β , and γ in this order. In the α -phase he found the two NH_3^+ and the two CH_3 stretching frequencies near 3000 cm^{-1} giving a broad feature in the spectrum and only two or three bands down to 2000 cm^{-1} . The band near 2000 cm^{-1} which we found in all the primary aliphatic amine hydrohalides is significantly absent from the spectrum in the α -phase.

Waldron was able to assign practically all the bands using the analogy with ethane. Under C_{3v} symmetry the antisymmetrical NH_3^+ and CH_3 stretching and bending vibrations and the NH_3^+ and CH_3 rocking vibrations are doubly degenerate and the torsional oscillation is forbidden, though it might appear in combinations. Actually in the α -phase no splitting of the degenerate bands occurs and the torsional oscillation is absent, indicating threefold symmetry. In the β -phase the torsional oscillation was found by Waldron at 487 cm^{-1} , a strong band appears at 2075 cm^{-1} and a series of sharp bands appear between 2800 and 2400 cm^{-1} . In the γ -phase the situation was similar but the torsional oscillation band was not actually found. The main point is that the low temperature phases have no threefold axis and therefore the degenerate bands split.

Now, it is very interesting that all our primary amine hydrohalide spectra closely resemble Waldron's low temperature spectra although they have all been measured at room temperature. The natural explanation is that because of the bulky groups linked to the nitrogen atom none of our compounds possesses C_{3v} symmetry nor a threefold axis.

TABLE I

(a) Cyclohexylamine				(b) Di- <i>n</i> -butylamine				(c) Triethylamine			
Free amine, liquid	Hydro- chloride	Hydro- bromide	Hydro- iodide	Free amine, liquid	Hydro- chloride	Hydro- bromide	Hydro- iodide	Free amine, liquid	Hydro- chloride	Hydro- bromide	Hydro- iodide
3355 m	3211 vw	3202 vw	3178 w		3173 sh	3138 sh	3140 sh			3169 vw	
3277 m	3106 vw	3093 vw	3070 w		2986 sh, broad	2988 sh, broad	3027 sh, broad			3049 vw	
3178 w	2975 sh	2980 sh, broad	2987 vs, broad	2950 s	2950 s	2950 s	2950 vs	2989 sh		2992 m	2998 sh
3088 vw	2948 sh	2952 sh	2963 s	2915 s	2923 s	2923 s	2915 vs	2967 s		2963 s	2961 s
2915 vs, broad	2920 vs	2925 sh	2925 sh	2865 s	2860 s	2860 s	2865 vs	2929 vs		2926 vs	2926 vs
2840 s	2807 s	2807 s	2809 s, broad	2853 s	2792 sh	2789 s	2789 s	2945 s		2968 vs	2878 s
2840 s	2850 s	2850 s	2848 s	2800 s	2780 m			2880 s		2874 s	2878 s
2740 vw	2828 m	2828 m	2804 m		2754 m	2744 sh	2735 sh	2808 s		2803 m	2815 vw
2696 vw	2775 m	2765 m	2752 m		2730 m	2730 sh	2698 sh	2805		2796 s	2787 m
2660 w	2722 m	2714 m	2698 m		2705 sh	2699 sh	2682 sh	vs		2761 m	2740 s
2589 vw	2668 m	2660 r	2642 m		2655 sh	2651 sh		2794		2731 s	2730 s
2611 m	2599 m	2599 m	2570 m		2626 sh	2620 sh	2620 sh	2751 sh		2660 sh	2668 vs
2564 m	2555 m	2555 m	2537 m		2602 sh	2555 sh	2547 w	2716 s		2633 sh	2633 sh
			2505 vw		2548 m	2537 m	2518 m	2706 sh		2613 s	2613 s
			2474 m		2531 sh	2516 sh	2492 m	2662 m		2604 s, broad	2590 w
			2454 w		2448 s	2431 s	2413 s	2638 m		2561 m	2562 vw
			1957 m		2385 m	2370 m	2359 m	2506 w			2520 m
	2050 m	2030 m									2520 m
1965 w	1965 w	1950 w									2486 s
											2482 s
											2425 w
											2270 vw
											2252 vw
											2248 vw
											2131 vw
											2126 vw

TABLE II

(a) Aniline				(b) Diphenylamine				(c) Pyridine			
Free amine, liquid	Hydrochloride	Hydrobromide	Hydride	Free amine, solid	Hydrochloride	Hydrobromide	Hydride	Free amine, liquid	Hydrochloride	Hydrobromide	Hydride
3433 vs				3400 vs	3104 vw	3082 w	3095 vw				3228 sh, m
3350 vs	3108 sh			3377 vs	3071 vw	3063 vw	3036 vw	3007 w	3208 w	3200 w	3200 m
3214 vs	3149 w			3175 m	3052 vw	3044 vw		3046 w	3100 sh	3135 sh	3137 w
				3096 s	3038 w	3030 w	3013 vw				
3100 sh	3063 m			3046 vs	3015 w	3011 w	2865 w	3015 w	3124 w	3119 sh	3114 sh, w
				3028 vs	2895 m	2880 m	2843 w				
3088 m	3036 m	3000 sh	2990 sh	2747 m	2842 m	2832 m	2820 w	2992 w	3092 vw	3085 sh	3075 w
3063 s	2810 s, broad*	2830 s, broad*	2870 s, broad*	2720 m	2795 m	2775 m	2770 w	2901 w		3061 sh	
				2651 m	2749 sh	2738 sh					
3025 vs	2631 sh	2600 sh, w		2532 m	2743 m	2723 m	2724 sh	2846 w	3043 m	3030 sh	3040 m
				2476 w	2722 w	2713 sh	2717 m				
2999 s	2583 m	2572 m	2555 m	2390 w	2700 m	2686 m			3010 m		
2949 w	2558 m	2546 m	2529 m		2673 m	2662 m	2663 sh				
2921 w	2418 w				2648 m	2638 m	2658 m*		2920 m	2908 w	2925 m, broad*
2900 w	2280 w				2607 sh	2605 sh	2592 m				
					2580 s	2575 s	2576 m				2870 sh
					2572 s	2550 s			2846 m	2842 w	2860 m, broad*
2705 w	2263 m				2474 sh	2498 m	2510 w		2713 w	2708 w	2718 w
						2464 sh	2498 w				
							2462 m*				

TABLE II (concluded)

(a) Aniline			(b) Diphenylamine			(c) Pyridine		
Free amine, liquid	Hydrochloride	Hydrobromide	Hydrochloride	Hydrobromide	Hydrobromide	Free amine, liquid	Hydrochloride	Hydrobromide
2727 w	2201 w		2455 vs	2447 m				2655 sh
2652 w	2163 w		2405 sh	2385 sh	2440 m			2685 sh
2620 w	2055 m		2344 sh, vs	2354 sh	2417 m			2605 s, broad* 2560 w
			2331 vs	2331 s	2401 sh		2580 sh	2582 sh
			2322 vs	2320 s*			2519 sh	
	2015 m		2280 vs*	2279 s	2283 vs			
1990 m	1990 m		2245 sh					
			2218 sh					
			2174 m	2107 w				2498 vw
			2156 m	2146 w				2460 vw
			2082 w	2071 w				2402 w
			2045 m	2030 m			2240 w	2233 w
			1985 m	1945 m			2159 vw	2152 vw
								2069 vw
							2091 m	2071 vw
							2005 m	

vs = very strong, s = strong, m = medium, w = weak, vw = very weak, * = "centre of gravity".

The band near 2075 cm^{-1} was assigned by Waldron to a combination band between the torsional oscillation (487 cm^{-1}) and the antisymmetrical bending vibration of the NH_3^+ group (1580 cm^{-1}); the sharp bands between 2800 and 2400 cm^{-1} were assigned to combinations between various NH_3^+ and other deformation bands. This can now be generalized to all the aliphatic primary amine hydrohalides whose spectra are reported here.

The sharp bands between 2800 and 2400 cm^{-1} generally accompany the strong combination band near 2000 cm^{-1} . The splitting of the former and the high intensity of the latter both appear to be connected with the lowering of symmetry, although the combination tone near 2000 cm^{-1} is allowed under C_{3v} symmetry. The lowering of the intensity of the bending bands in the 1600 – 1500 cm^{-1} area found by Waldron seems to be a related phenomenon.

The characteristic shift toward lower frequencies of the bands between 2800 and 2400 cm^{-1} in the order $\text{Cl} \rightarrow \text{Br} \rightarrow \text{I}$ is definitely confirmed by our new measurements and is explained making use of the above assignments. This shift is in the NH_3^+ deformation bands. The NH_3^+ stretching bands should then shift in the opposite direction giving the strongest hydrogen bond with the chloride ion and the weakest with the iodide ion. Unfortunately it is quite impossible to establish this prediction because of the considerable amount of band overlap which takes place in the 3000 cm^{-1} region. The cyclohexylamine salts give relatively the best chance of resolving the NH_3^+ stretching bands since there we have only CH_2 groups, and no CH_3 groups. In fact the cyclohexylamine hydriodide has the NH_3^+ bands well separated from the CH_2 bands while the hydrobromide and hydrochloride give only strong shoulders. A consideration of the spectra of the N-deuterated and perfluoro-alkyl analogs could solve this problem and work is going on in this laboratory in this direction.

The above interpretation is, however, in line with our findings on amine salts of other classes and therefore seems very probably correct (see below).

The band near 2000 cm^{-1} shifts in the same direction but more rapidly in the hydrohalide series $\text{Cl} \rightarrow \text{Br} \rightarrow \text{I}$ than do the upper sharp bands. This must be due to the fact that its two components shift individually in the same direction.

There are two or three weak bands above the NH_3^+ stretching bands up to about 3200 cm^{-1} . These can be readily assigned to the first overtones of the bending vibrations located in the 1600 – 1500 cm^{-1} area or to a combination of them.

The interpretation of the sharp bands between 2800 and 2400 cm^{-1} as combination tones involving deformation modes (which differs from the assignment suggested in paper I) appears to be the key to the understanding of these spectra. Indeed, their characteristic shifting with different hydrohalides provides us with a method of distinguishing between $\text{N}^+-\text{H}-\text{X}^-$ stretching bands and deformation bands. Combinations involving $\text{C}-\text{H}$ or $\text{C}-\text{C}$ vibrations should be distinguishable as well, since these should shift very little, or not at all, when the type of hydrohalide is varied from hydrochloride to hydriodide.

(B) Aliphatic Secondary Amine Salts

In the spectra of the secondary amine salts the NH_2^+ stretching bands are found at lower frequencies overlapping the CH_3 and CH_2 stretching bands from the low frequency side.

The situation is not entirely clear, however, because of the high degree of overlapping.

There are no bands near 2000 cm^{-1} in the spectra of diethylamine and di-*n*-butylamine hydrohalides. In piperidine hydrohalides there are two or three weak bands in this part of the spectrum and at the same time a greater number of sharp bands appear in the $2800\text{--}2400\text{ cm}^{-1}$ region. The bands near 2000 cm^{-1} are probably due to combinations between the $\overset{+}{\text{N}}\text{H}_2$ bending vibration below 1600 cm^{-1} and some low frequency vibration. Proof should come from the low frequency part of the spectrum.

The bands of the secondary amine hydrohalides tend to be somewhat broader than those of the primary amine hydrohalides.

(C) Aliphatic Tertiary Amine Salts

As was stated in paper I, the center of gravity of the broad $\overset{+}{\text{N}}\text{H}$ absorption region of the hydrohalides of a given tertiary amine shifts towards higher frequencies in the order $\text{Cl} \rightarrow \text{Br} \rightarrow \text{I}$. This shift is in the reverse direction to that of the sharp bands between 2800 and 2400 cm^{-1} in the primary and secondary amine salts.

In all likelihood this absorption region is due to the $\overset{+}{\text{N}}\text{H}$ stretching band. Then it can be seen that since the hydrochloride has the lowest $\overset{+}{\text{N}}\text{H}$ stretching frequency the chloride ion gives the strongest hydrogen bonds.

The centers of the bands are at considerably lower frequencies than are the $\overset{+}{\text{N}}\text{H}$ stretching frequencies in the primary and secondary amine hydrohalides, being found at about 2600 and 2450 for the hydrochlorides of triethylamine and tri-*n*-butylamine respectively. Although we do not know exactly the frequency range of the unassociated $\overset{+}{\text{N}}\text{H}$ stretching band, it is quite clear that tertiary amine hydrohalides form stronger hydrogen bonds than do the primary and secondary amine salts. This is consistent with the fact that in this case the positive charge is distributed only between the nitrogen atom and one hydrogen atom, rather than two or three hydrogen atoms.

No broad bands appear in superposition with the CH_3 and CH_2 stretching bands in the tertiary amine salt spectra and this further confirms the assignment of the $\overset{+}{\text{N}}\text{H}$ stretching band in all these cases.

There are a great number of sharp bands superimposed on both sides of the main band center, and it is significant that those sharp bands which can be followed hydrochloride to hydrobromide to hydriodide exhibit a slight shift toward lower frequencies in the order $\text{Cl} \rightarrow \text{Br} \rightarrow \text{I}$ just as do the sharp bands in the primary and secondary aliphatic salts.

This shows again that these are combination bands involving $\overset{+}{\text{N}}\text{H}$ deformation bands and that the broad stretching band shifts in the opposite direction. Other bands of similar origin are in coincidence with the broader $\overset{+}{\text{N}}\text{H}$ stretching bands and it is difficult to follow their shifting.

As expected, no band appears near 2000 cm^{-1} , since there is no possibility of torsional oscillations of the tertiary amine group.

(D) Aromatic Primary Amine Hydrochlorides

The two main bands in aniline hydrochloride have their maxima at 2810 and 2570 cm^{-1} respectively, the upper one having a strong shoulder on the high frequency side. In the two other salts the separation is even larger. Since in the aliphatic case the antisym-

metrical and symmetrical NH_3^+ stretching vibrations are almost coincident, it seems to be unlikely that the two main maxima in aniline hydrochloride correspond to these bands.

The upper maximum of aniline hydrochloride shifts toward higher frequencies in the order $\text{Cl} \rightarrow \text{Br} \rightarrow \text{I}$ but less than in the case of the tertiary amine hydrohalides. The lower maximum (with two peaks), however, shifts toward lower frequencies showing that these are not NH_3^+ stretching bands but combination bands involving fundamentals of NH_3^+ deformation vibrations and that the upper band which is stronger and broader must contain the two or three NH_3^+ stretching frequencies. There is a close analogy here with the "satellite" bands of carboxylic acid dimers discussed by Bratož, Hadži, and Sheppard (9).

As was pointed out in paper I, since aniline is a very weak base, it is possible that we have two potential minima of comparable depths for the hydrogen-bonded NH_3^+ stretching motions with a low barrier between them. If this is the situation, tunnelling of the proton may occur and the NH_3^+ stretching bands (or rather only the antisymmetrical one) (see ref. 3) may split. Blinc and Hadži (10) interpreted in this fashion the spectra of KH_2PO_4 -type compounds and Detoni and Hadži (11) those of sulphinic acid.

A similar explanation, however, could hardly explain the two main bands of the aniline hydrohalides. It would be contradicted by the above described shifting of these bands and it is rendered improbable, too, by the large separation between them. A splitting by double-well mechanism is still possible if both bands resulting from the splitting are contained in the broad upper band. There is more indication for this in the spectra of α and β naphthylamine salts which otherwise resemble the spectrum of aniline. More work is needed to elucidate this problem.

The main point is that these spectra actually resemble the aliphatic analogues more closely than it may appear at first sight and follow the same general pattern.

In all the aromatic primary amine *hydrochlorides* there is a strong combination tone near 2000. Comparison with the amines themselves shows that these are unlikely to belong to the well-known combination bands of the aromatic compounds (12). However, torsional oscillations should be again possible in these cases.

(E) Aromatic Secondary Amine Hydrohalides

Diphenylamine hydrohalides have interesting spectra. The main band is at much lower frequencies than it is in aniline. Again the center of gravity shows the upward shift in going from Cl^- to I^- but the other sharp bands show the downward shift.

Surprisingly there is a well-formed doublet in the 2000 cm^{-1} area. This may be a combination between some low frequency vibration and the NH_2^+ bending band near 1550 cm^{-1} .

The N-methylaniline hydrohalide spectra show the same general features but the NH_2^+ stretching bands are in the 2800 cm^{-1} region.

(F) Aromatic Tertiary Amine Hydrohalides

N-Methyl diphenylamine and pyridine give very strong hydrogen bonds; N,N-dimethylaniline gives somewhat weaker ones, probably for steric reasons.

The centers of gravity of the NH^+ stretching bands move upwards (except in the case

of *N,N*-dimethylaniline where the hydrochloride and hydrobromide have NH^+ stretching bands at about the same place), and the sharp bands show the above described slight downward shift.

The NH^+ stretching bands in this group of salts are at rather low frequencies and this shows again that weak bases and tertiary bases form the strongest hydrogen bonds and that this is accompanied by greatly broadened bands.

The two bands in pyridine salts near 2000 cm^{-1} constitute a difficult problem. We tentatively assign them to combination tones usually found in spectra of aromatic compounds.

We see that the spectra of aromatic amine hydrochlorides differ from the aliphatic salts inasmuch as the hydrogen bonds are usually stronger and the bands are broader in the former, but the differences are not really of a fundamental nature.

DISCUSSION AND CONCLUSIONS

Among the factors which determine the energy of a hydrogen bond are the following: attractive electrostatic forces operating in an $\text{X}-\text{H}\cdots\text{Y}$ system, repulsions between the end atoms, and delocalization of the Y lone pair and $\text{X}-\text{H}$ bonding electrons (13, 14, 15). The usually high intensity of hydrogen-bonded $\text{X}-\text{H}$ stretching bands is explained by considering the variation of bond polarity during the vibrational motion and the increasing amount of delocalization when the bond is shortening (16, 17).

Concerning the energy of the hydrogen bond we suggest that in the case of amine hydrohalides it is largely electrostatic as would be expected because of the presence of net charges. The amount of positive charge left on the hydrogen-bonded protons is important in determining shifts going from hydrochlorides to hydrobromides and hydriodides. This was treated in more detail in paper I.

Although the absolute intensities were not measured, it was observed that the amine hydriodides have usually the weakest spectra. Since delocalization would give them the highest intensity this is further evidence that these hydrogen bonds are largely electrostatic in character.

The width of the bands and the appearance of many bands when hydrogen bonding is present are certainly the most interesting of the related problems and have received much attention. It has been suggested that the great anharmonicity of the potential surfaces is the cause of the appearance of many overtones and combination tones (18). The importance of anharmonicity for the various phenomena connected to hydrogen bonding cannot be overestimated. It is, however, very likely, as Bratož and Hadži pointed out, that only the parts of the potential surface pertaining to the XH stretching vibrations are very anharmonic and that the parts pertaining to the bending vibrations are only slightly anharmonic. It might, therefore, be suggested that those combination bands which are found in the XH stretching region accompanying the "real" XH stretching bands should be combinations between the latter and some other bands of lower frequency. This is, however, obviously not the case. In Waldron's interpretation of methylamine hydrochloride all the bands around the broad "real" stretching bands are overtones or combination tones involving bending vibrations. This is confirmed by the present results and especially by the direction of the frequency shift from hydrochloride to hydrobromide to hydriodide of all the sharper bands, which is in the opposite sense from that occurring

for the broad true NH^+ stretching bands. Bratož, Hadži, and Sheppard (9) reached similar conclusions for carboxylic acid dimers and Newman and Badger for certain amides (19).

Combination tones due to deformation vibrations may coincide with the "real"

hydrogen-bonded stretching band and broaden and complicate it further. This is the case in the spectra of many secondary and tertiary amine hydrohalides. In other cases they may appear non-coincident giving a clearer spectrum as in ammonium salts and primary aliphatic amine hydrohalides.

If the sharp bands which appear in the NH^+ stretching region were interpreted as combinations between the "real" stretching bands and some low frequency band (possibly the series of harmonics of the XY bridge frequency) then they would have to be difference tones and thus they should disappear or become very weak at low temperatures. Waldron's work shows quite clearly, however, that this does not happen.

The pronounced ability of the bending bands to form combination tones may appear unusual because of the low mechanical anharmonicity of the deformation vibrations involved. (Fermi resonance could only be involved to explain their relatively high intensities where they fall close to the NH^+ stretching bands; this, however, is very often not the case.) It is interesting to note in this respect that the free amines, which form only weak hydrogen bonds, exhibit a few such bands in the $2800\text{--}2400\text{ cm}^{-1}$ area (see Tables I and II). It seems likely, therefore, that the mechanical anharmonicity of the potential curve due to hydrogen bonding is not the main cause of the appearance of these combination bands. Since the only other factor which might cause them to appear is electrical anharmonicity, we conclude that this latter effect must be very important in hydrogen-bonded molecules especially for bending vibrations, and that it is responsible for much of the fine structure. W. E. Thompson and Pimentel (20) reached similar conclusions in a study of the association between chloroform and cyclohexylamine.

RÉSUMÉ

Les spectres infrarouges d'un certain nombre d'halogénures d'amine ont été mesurés.

La formation de liaisons hydrogène et les oscillations torsionnelles des groupements NH_3^+ influencent ces spectres d'une manière caractéristique. Les vibrations de valence du groupe $\text{N}^+\text{--H}\cdots\text{Y}^-$ donnent des bandes larges ou assez larges. Elles se trouvent autour de 3000 cm^{-1} chez les sels des amines aliphatiques primaires. Elles apparaissent à des fréquences un peu plus basses chez les sels d'amines secondaires et beaucoup plus basses chez les tertiaires. Les sels halogènes des amines aromatiques ont ces bandes à des fréquences plus basses que les sels d'amines aliphatiques de la même catégorie.

Il y a un déplacement vers les hautes fréquences dans l'ordre chlorhydrate, bromhydrate, iodhydrate.

Tous ces spectres contiennent un certain nombre de bandes plus minces qui coïncident ou non avec les bandes de valence $\text{N}^+\text{--H}\cdots\text{Y}^-$. Ce sont des tons de combinaison faisant intervenir des modes de déformation. Ils se déplacent vers les fréquences basses dans l'ordre chlorhydrate, bromhydrate, iodhydrate.

L'importance de l'anharmonicité électrique faisant apparaître ces bandes est soulignée. L'énergie de la liaison hydrogène vient surtout de contributions électrostatiques.

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COMPLEX COBALT PERIODATES¹

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ABSTRACT

A number of complex cobalt periodates have been prepared. Sodium periodatocobaltate (III) $\text{Na}_3\text{H}_2\text{Co}(\text{IO}_6)_2 \cdot 10\text{H}_2\text{O}$ is obtained as green crystals when cobaltous and periodate ions react in the presence of alkaline sodium hypochlorite. Somewhat similar potassium, barium, and lanthanum salts are described. Various methods of demonstrating that the cobalt is trivalent, including the observation that sodium periodatocobaltate (III) is diamagnetic, are described. The free acid $\text{H}_7\text{Co}(\text{IO}_6)_2$ can be obtained in solution, and measurements have been made on its ionization constants. Observations have been made on the stability of these compounds, and the stability constant of the periodatocobaltic ion (in alkaline solution at 60°C) has been shown to be in the neighborhood of 10^8 .

Some years ago one of the writers of this paper noted that complex periodates of trivalent copper could be prepared by oxidizing divalent copper to trivalent copper by means of sodium hypochlorite in the presence of sodium or potassium periodate (1). The compounds so obtained were the same as those prepared earlier by Malatesta, using persulphate oxidation (2). Evidence for the existence of the copper complexes and measurements on their stability were obtained from the fact that copper was a much less efficient catalyst for the decomposition of sodium hypochlorite if periodate was present; the complex salt did not catalyze this reaction while uncomplexed copper did. It was noted at the same time that the catalysis by cobalt salts was also much decreased if periodate was present, and this suggested that a similar cobalt compound might be formed. The present paper describes the preparation of compounds of this sort, and gives a description of some of their properties.

(1) Preparation of Compounds

(i) Sodium Periodatocobaltate (III)

The general method used to prepare sodium periodatocobaltate (III) was as follows: cobalt sulphate (or chloride) solution was mixed with sodium periodate and enough dilute sulphuric acid to dissolve this relatively insoluble salt. The mixture was then poured into a considerable excess of alkaline sodium hypochlorite with vigorous stirring. A dark green precipitate formed, which was centrifuged off, washed with a little cold water, and then largely redissolved in dilute sodium hydroxide. The solution was filtered, and the complex periodate reprecipitated by adding alcohol. It was then filtered off, washed, and dried.

In some cases the initial precipitate was small in size and almost black (probably containing mostly cobalt (III) hydroxide). If this was filtered off, the filtrate was dark green and slowly deposited green crystals of the complex periodate. In every preparation, considerable loss of yield was caused by precipitation of cobalt (III) hydroxide, and it was essential to recrystallize the product to free it from this compound.

In a typical preparation, 14 g of sodium periodate, $\text{Na}_2\text{H}_3\text{IO}_6$, was dissolved in 75–100 ml of water with a minimum of nitric acid present to effect solution. Five grams of cobalt chloride hexahydrate was added. Meanwhile, 15 g of sodium hydroxide was dissolved in 50 ml of 1.5 M sodium hypochlorite. The two solutions were mixed, and the green precipitate was separated by centrifuging. The precipitate was washed with a little cold water, and then stirred into 400 ml of dilute (about 0.1 M) sodium hydroxide. The

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insoluble portion was filtered off, and alcohol was added to the filtrate. The sodium periodatocobaltate (III) precipitated. The yield after a further recrystallization was 3.7 g.

(ii) *Analysis*

The method of analysis was as follows. A weighed sample was dissolved in water, and enough sulphur dioxide was bubbled in to cause complete reduction to iodide. The solution was briefly boiled to remove excess sulphur dioxide, and silver nitrate was added in excess. The precipitated AgI was filtered off, dried at 100° C, and weighed. This gives the iodine content. Excess potassium iodide was added to the filtrate, and silver iodide was filtered off. Cobalt was precipitated from the filtrate, either as cobalt anthranilate or as cobalt sulphide by ammonium carbonate and hydrogen sulphide. In the latter case the precipitate was digested with sulphuric acid, evaporated, and the residue of CoSO_4 was weighed. For sodium, a sample was dissolved in aqueous sulphur dioxide as before, and the cobalt removed as sulphide. The filtrate was evaporated with a little sulphuric acid, and the residue (after treatment with ammonium carbonate to remove NaHSO_4) was weighed as Na_2SO_4 .

A second, more convenient, method was developed later. The sample was reduced by sulphur dioxide, the excess being boiled off as before. The solution was passed through a column of a cation exchange resin (14 cm long by 1 cm diameter of Dowex 50S-X8 in 50–100 mesh) in its hydrogen form. The effluent contains the iodide, which was estimated as AgI as before. The resin was eluted with 0.4 N HCl which removes the sodium. This liquid was then evaporated, and the residue of NaCl weighed. Finally the resin was eluted with 2 N HCl which removes the cobalt, and this was converted to the anthranilate or sulphate for weighing.

The water in the sample was measured by the loss in weight at 150° C.

The result of a typical analysis follows. Found: Na, 14.3; Co, 7.33; I, 31.25; H_2O , 22.3%. Theoretical for $\text{Na}_5\text{H}_2\text{Co}(\text{IO}_6)_2 \cdot 10\text{H}_2\text{O}$: Na, 14.34; Co, 7.35; I, 31.65; H_2O , 22.47%.

In many samples the cobalt was a little high (up to about 8%), presumably because of contamination by cobalt hydroxide.

Another check on the sodium content was made by passing a solution of sodium periodatocobaltate (III) through an anion exchange resin in its chloride form. The complex displaces chloride into the effluent solution, and by using known amounts of the complex it was found that five chlorides (measured by silver nitrate titration) were displaced by 1 molecule of complex.



where R represents the ion exchange resin.

Further evidence supporting this formula will be given later.

(iii) *Potassium Periodatocobaltate (III)*

A very similar compound was obtained using the potassium instead of the sodium salts in the method given above. The potassium compound, however, is more soluble than the sodium salt, so it needed more alcohol to precipitate it. The salt, after being dried over calcium chloride, is hygroscopic, and readily picks up water, at least in humid weather. An alternative method was to pass the sodium salt in solution through a cation exchange resin in its hydrogen form, when free periodatocobaltic acid is obtained. This was then neutralized by potassium hydroxide, and precipitated with alcohol.

The analysis, done by the same methods as for the sodium salt, gave as follows. Found: K, 22.6; Co, 8.60; I, 32.8; H_2O , 7.45%. Calc. for $\text{K}_4\text{H}_3\text{Co}(\text{IO}_6)_2 \cdot 3\text{H}_2\text{O}$: K, 21.8; Co, 8.21; I, 35.3; H_2O , 7.52%. This preparation was made in somewhat less alkaline solution than

for the sodium salt, which may account for the lower alkali metal content. Like the sodium salt, this compound gave small green crystals.

(iv) *Barium Periodatocobaltate* (III)

The barium salt was prepared in various ways, and gave different compounds depending on the conditions. Firstly, the sodium salt was converted into the free acid by passing through a cation exchange resin in its hydrogen form. The free acid was neutralized to pH = 11.5 by carbonate-free sodium hydroxide, and then barium chloride solution was added. This was done under nitrogen to avoid contamination with barium carbonate. A green precipitate formed which was filtered off, washed, and dried. The analysis was as described above, except that the barium was weighed as BaSO₄. The results were as follows. Found: Ba, 37.5; Co, 6.55; I, 25.8; H₂O, 9.58%. Calc. for Ba₃[H₂Co(IO₆)₂ · 10H₂O: Ba, 36.5; Co, 6.27; I, 26.9; H₂O, 9.51%.

In acid solutions a different precipitate was obtained. If the free complex acid (pH about 2.5) was mixed with barium chloride solution, a green precipitate was formed of rather variable composition. It gave a Ba/Co ratio of close to one, but the iodine content was lower than that expected if the I/Co ratio is 2 as in the compounds described above. Several samples gave analyses close to Ba₂H₃Co₂(IO₆)₃ · 5H₂O. However, the results were sufficiently variable that it cannot be considered that this has been established as a definite compound.

(v) *Lanthanum Periodatocobaltate* (III)

This compound was prepared by converting 1.6 g of the sodium salt to the free acid by cation exchange, and adding 50 ml of 0.1 M lanthanum nitrate. The green precipitate analyzed as follows. Found: La, 21.0; Co, 9.28; I, 29.7; H₂O, 16.4%. Calc. for La₂Co₂H₃(IO₆)₃ · 12H₂O: La, 21.6; Co, 9.18; I, 29.7; H₂O, 16.8%.

It is interesting to note that another iodine-to-cobalt ratio is present. Possibly the lanthanum as another trivalent atom is capable of taking the place of cobalt in the compound.

At high pH (by adding lanthanum nitrate to the sodium complex) the green precipitate, however, had approximately the 2:1 ratio for iodine to cobalt found in the sodium complex. The analyses most nearly agreed with La₄[H₃Co(IO₆)₂]₃ · 18H₂O. However, no way of recrystallizing this compound (or the barium compounds) was found, for it is insoluble in water, and decomposed by acids.

(2) *Valency of Cobalt*

In the formulae quoted above it was assumed that the cobalt was trivalent. This is certainly the valency that one would expect for cobalt complexes formed under oxidizing conditions. However, these formulae are supported by various experimental results, which will now be given.

(i) *Oxidation of Iodide*

It was found that the corresponding copper compounds oxidized iodide ions in acid solution. The amount of iodine liberated depended on whether the acid was added before or after the iodide. If the iodide was added first, the copper was reduced by it from copper (III) to copper (I). If acid was added first, it decomposed the compound to give copper (II), and later addition of iodide only reduced copper (II) to copper (I). Hence, in the latter case less iodine was liberated, and from the ratio of the amounts the valency of the copper in the original compound could be deduced.

The same method was applied to sodium periodatocobaltate (III). The difficulty here is that the complex acid is so stable that prolonged boiling with acid is needed to decompose

it. However, it can be done, and then on adding iodide the cobalt remains as Co(II) and only periodate is reduced. If iodide is added first, the equivalent weight of sodium periodatocobaltate (III) is 1/17 of its molecular weight (eight iodines are liberated for each periodate, and one for Co(III) to Co(II)).

The observed equivalent weights were:

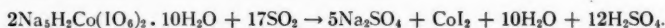
(1) Potassium iodide added first, obs. equivalent weight = 47.0, calc. equivalent weight = 47.15 (mol. wt./17).

(2) Acid added first, obs. equivalent weight = 50.7, calc. equivalent weight = 50.1 (mol. wt./16).

These results support a formula with trivalent cobalt.

(ii) *Reduction by Sulphur Dioxide*

A rather similar experimental confirmation comes from the reduction of the compound by aqueous sulphur dioxide. Here the sulphur dioxide is oxidized to sulphuric acid, and after unused sulphur dioxide has been boiled out, the acid can be titrated with sodium hydroxide. If bromocresol green is used as indicator, the cobalt ions do not interfere in the titration. It was found that 1 g-equivalent of sulphuric acid was produced by 67.0 g of the compound. The weights calculated for different cobalt valencies are: Co(II) 73.0; Co(III) 66.8; Co(IV) 61.6. Hence these results support trivalent cobalt, and the equation for the reduction is:



(iii) *Reduction by Ferrous Sulphate*

Sodium periodatocobaltate (III) can be titrated with ferrous sulphate in acid solution. A solution of the complex salt in about 1.0 *N* sulphuric acid was used, and the titration was followed potentiometrically. The cell used was: Pt/ $\text{Na}_5\text{H}_2\text{Co}(\text{IO}_6)_2$ in acid/ Hg_2Cl_2 in saturated KCl/Hg. With more dilute sulphuric acid (about 0.1 *N*), some precipitate formed in the early part of the titration, and the results were somewhat erratic. Sodium periodate also gives a similar titration, and it is then reduced to sodium iodate; some results of this titration are given for comparison. The results given below are the voltages relative to the saturated calomel electrode, so -0.242 v (3) must be added for voltages relative to the standard hydrogen electrode.

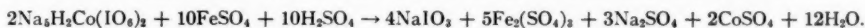
(a) Titration of 0.00503 *M* sodium periodatocobaltate (III) in 1.0 *N* sulphuric acid against 0.0913 *M* ferrous sulphate at 25° C. Moles Fe^{++} /moles $\text{Na}_5\text{H}_2\text{Co}(\text{IO}_6)_2$ and e.m.f. (volts): 0 (-1.023), 0.91 (-1.023), 1.82 (-1.019), 2.72 (-1.006), 3.18 (-1.002), 3.63 (-0.996), 3.99 (-0.987), 4.36 (-0.962), 4.72 (-0.889), 5.08 (-0.770), 5.45 (-0.675), 5.81 (-0.617), 6.17 (-0.584), 6.53 (-0.569), 7.26 (-0.556), 9.08 (-0.549).

(b) Titration of sodium periodate in 1.0 *N* sulphuric acid at 25° C. Moles Fe^{++} /moles $\text{Na}_2\text{H}_3\text{IO}_6$ and e.m.f. (volts): 0 (-1.045), 0.49 (-1.041), 0.98 (-1.031), 1.38 (-1.002), 1.57 (-1.016), 1.77 (-1.012), 1.97 (-0.732), 2.16 (-0.619), 2.36 (-0.588), 2.56 (-0.577), 2.95 (-0.570), 4.91 (-0.560).

In the second titration the voltage at the point where the periodate is half reduced is -1.033, or -1.275 relative to a standard hydrogen electrode. This is lower than Abel and Smetana's (4) result for this potential (-1.51 v), or Latimer's (5) estimate of it from the chemical behavior of periodic acid. Only about 0.05 v of this discrepancy can be attributed to partial ionization of the periodic acid. It seems probable that the electrode did not take up the true equilibrium potential for this system. Similarly, the apparent standard electrode potential for the reduction of the complex ion is between -1.19 and

-1.20 v relative to hydrogen, but again this may not be the true equilibrium potential. A reaction of this sort involving transfer of oxygen may well be a slow reaction.

However, the number of molecules of ferrous sulphate reacting is quite definite. The inflection occurs at 2 molecules for sodium periodate (i.e. reduction to iodate) and 5 for sodium periodatocobaltate (III). This is what is required for trivalent cobalt:



(iv) *Magnetic Properties*

Measurements were made of the magnetic susceptibility of the sodium compound, by means of a Gouy apparatus of the conventional type. Both the solid and an aqueous solution were used. The results in aqueous solution cannot be very accurate, since the sodium periodatocobaltate (III) is not very soluble in water, and hence a dilute solution had to be used. The results made $\chi = -570(\pm 100) \times 10^{-6}$ per g-molecule of compound, from the solution measurements.

In the solid state, the degree of purity of the sample had a considerable effect on the result, the sample becoming more diamagnetic as it was recrystallized. It is evident that most samples contain traces of a paramagnetic impurity, probably cobalt oxide. The purest sample gave a susceptibility of -290×10^{-6} /g-molecule. It is difficult to make a precise theoretical calculation for this number, since the contributions of the atoms, particularly the iodine in this valency state, are not too certain. However, Angus's expression (6) predicts a value of about -350×10^{-6} /g-molecule. In any case it is clear that the compound is diamagnetic, as is generally found for Co(III) compounds.

(3) *Spectrum of Sodium Cobalt Periodate and of Periodate-cobaltic Acid*

Solutions of sodium periodatocobaltate (III) are green. The absorption spectrum shows a maximum at $625 \text{ m}\mu$, and a minimum at $535 \text{ m}\mu$. The absorption rises steadily towards the violet and falls towards the red. Values for the extinction coefficients, measured on a $5 \times 10^{-3} \text{ M}$ aqueous solution by means of a Beckmann D.U. spectrophotometer, are for sodium periodatocobaltate (III), λ (ϵ): 320 (2340), 340 (1440), 360 (1085), 380 (687), 400 (550), 420 (389), 440 (275), 460 (206), 480 (153), 500 (100), 510 (79.5), 520 (69), 530 (64), 540 (64.5), 550 (68.5), 560 (75.5), 580 (93), 600 (108), 610 (111.5), 620 (112.5), 630 (113), 640 (109), 650 (103), 675 (75.5), 700 (47), 750 (17), 800 $\text{m}\mu$ (11). The absorption in the violet starts at much longer wave lengths than does the similar absorption of periodate ions alone. KH_2IO_6 , λ (ϵ): 260 (320), 280 (236), 300 (150), 320 (45), 340 $\text{m}\mu$ (4). $\text{K}_2\text{H}_2\text{IO}_6$, λ (ϵ): 290 (395), 300 (272), 310 (182), 320 (113), 340 (35), 360 $\text{m}\mu$ (8).

In acid solution the spectrum is somewhat altered. This change seems to take place in at least two stages. If acid (HClO_4) is added, and the spectrum is rapidly measured, it is found to be as follows, $3.35 \times 10^{-3} \text{ M}$ sodium periodatocobaltate (III) in $3.35 \times 10^{-2} \text{ M}$ perchloric acid, λ (ϵ): 450 (193), 460 (162.5), 480 (116.5), 500 (87.5), 520 (70.5), 540 (67.5), 560 (73), 580 (85), 590 (88), 600 (90.5), 610 (91), 620 (90.5), 630 (87.5), 650 (76), 675 (57), 700 (38), 750 (18), 800 $\text{m}\mu$ (12). The maximum is shifted to $610 \text{ m}\mu$, and the maximum and minimum are less well marked. After this initial rapid change a slow further change occurs which will be considered in the next section on the stability of these compounds.

(4) *Stability of Sodium Periodatocobaltate (III) and of Periodatocobaltic Acid*

(i) *Stability of Free Acid*

If sodium copper (III) periodate is acidified, decomposition rapidly occurs to give Cu^{++} ions. It was expected that a similar reaction might occur with cobalt. However, the

acid proved much more stable, and required at least several hours of boiling with dilute sulphuric acid to give fairly complete decomposition to Co^{++} ions. At room temperature, solutions of periodatocobaltic acid (obtained by passing a solution of the sodium periodatocobaltate (III) through the hydrogen form of a cation exchange resin) can be kept for months.

As mentioned above, the absorption spectrum at first changes very rapidly if a solution of the sodium salt is acidified with perchloric acid. After this there is a further, moderately slow, change, taking place over a time of the order of 100 minutes at room temperature. This second stage in the decomposition is not simply decomposition to Co^{++} ions, as the spectrum after it has occurred is still fairly similar to that of sodium periodatocobaltate, and the rate of the process is much faster than that of the formation of Co^{++} . The rate of this second stage was examined a little more closely. Since the color change at any wave length is quite small (e.g. in one sample the color density changed from 0.381 to 0.353), it was only possible to get a rough measurement of the rate. If we assume that one colored species is slowly turning into another, and that the extent of the change is proportional to the change in the optical density, then the results indicate that this is a first-order reaction, with a rate constant about 0.03 min^{-1} at 30°C . The rate is very little affected by the hydrogen ion concentration, and has a fairly low temperature coefficient. Since the precise nature of this change is unknown, it did not seem to be worth while to get more than a rough estimate of its speed.

(ii) *Dissociation of Sodium Periodatocobaltate (III)*

In the work on the copper complexes referred to above it was possible to measure the stability of the complex (i.e. the equilibrium constant of the reaction: complex \rightleftharpoons copper + periodate ions) by measuring the rate of oxygen evolution from sodium hypochlorite solution containing various amounts of copper and periodate. It was assumed that only the simple copper ions acted as a catalyst of this decomposition, and this assumption led to consistent values of the equilibrium constant.

An attempt to make similar measurements with the cobalt compound encountered difficulties. In the first place, if relatively small amounts of a cobalt salt and a periodate are added separately to a solution of sodium hypochlorite, some of the cobalt always remains as the black insoluble cobaltic oxide. This causes relatively rapid oxygen evolution. This cannot be considered to prove that the equilibrium is much in favor of the simple ions, since, if sodium periodatocobaltate (III) solution is added, almost no gas is evolved as a result. It seems reasonable to assume that the very insoluble cobaltic oxide reacts so slowly that equilibrium is not reached. With copper, on the other hand, the metal is present as the soluble NaCu(OH)_4 . Whether equilibrium is reached when a solution of sodium periodatocobaltate (III) is added is uncertain; that is equilibrium for the reaction: $\text{Co(HIO}_6)_2^{-5} \rightleftharpoons \text{Co}^{+3} + 2\text{HIO}_6^{-4}$. The most that can be said is that no precipitate appears, and the rate of oxygen evolution does not rise appreciably with time.

The increase in the rate of gas evolution when the cobalt complex was added is so small that only a very rough value for this equilibrium constant can be obtained by this method. For instance, a solution containing an average concentration (during the measurement) of sodium hypochlorite of 1.495 M evolved oxygen at the rate of $0.1778 \text{ ml (at S.T.P.)/min}$ per liter of solution, when its temperature was 60°C . When the solution was made $6.52 \times 10^{-5} \text{ M}$ in sodium periodatocobaltate (III), the rate of evolution was $0.1696 \text{ ml (S.T.P.)/min}$ per liter; the average concentration of sodium hypochlorite was 1.416 M . The rate/ $[\text{ClO}^-]$ is 0.1189 without sodium periodatocobaltate (III), and 0.1199 with it. The weight of cobalt which would produce this increase can be

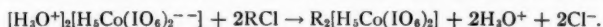
calculated from earlier data (7), and is 7.5×10^{-7} g of uncomplexed cobalt. From the volume of solution (767 ml) the concentration can be obtained, and as two periodates are combined with each cobalt, the equilibrium constant can be calculated. The result is $K = [\text{complex}]/[\text{Co(III)}] \cdot [\text{periodate}]^2 = 3 \times 10^{18}$. Other measurements gave somewhat lower values (down to 3×10^{17}); the cause of this lack of consistency is undoubtedly the very small differences (e.g. 0.004 ml/min) in the rate of oxygen evolution due to the cobalt compound.

However, it is plain that the cobalt compound is more stable than the copper compound where the corresponding equilibrium constant is 1.25×10^{10} at 40°C . For sodium periodatocobaltate the constant is in the neighborhood of 10^{18} at 60°C . These measurements are for dilute alkaline (about 0.1 M) solution, in which the precise chemical form of the uncomplexed cobalt is uncertain.

(5) pH Measurements

Since periodatocobaltic acid is reasonably stable, measurements were made to discover its ionization constants, and its general behavior in acid base titrations.

A solution of the free complex acid was prepared by passing the sodium salt through the hydrogen form of a cation exchange resin. The solution was 3.35×10^{-3} M and had a pH of 2.25 measured on a Beckmann pH meter with glass electrode. This makes the hydrogen ion concentration (or activity) 5.6×10^{-3} . This is not far off two hydrogen ions per molecule, so the first two ionization constants must be fairly large (if the first two ionization constants were the same, they would both have to be 1.0×10^{-2} to give the above pH). This conclusion is supported by the fact that when a solution of the free complex acid was run through an anion exchange resin (Dowex 1-X4) in its chloride form, slightly above two chlorides were displaced per molecule of periodatocobaltic acid:



Under similar conditions phosphoric acid liberated 0.90 chloride per molecule ($\text{p}K_1 = 2.12$).

On titrating periodatocobaltic acid with sodium hydroxide the curve in Fig. 1 was obtained. This has inflections at 2 and at 4 NaOH added per molecule. The first inflection

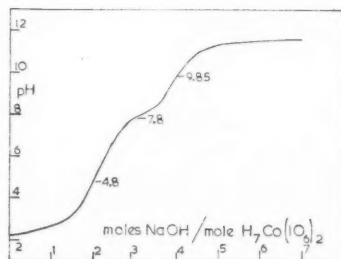


FIG. 1.

(2NaOH) is at a pH of 4.8, and the most horizontal part of the curve, between 2 and 4 NaOH is at a pH of 7.8. Since the pH at an inflection point is the mean of the $\text{p}K_a$ values on either side of it, the inflection at 2NaOH makes $\text{p}K_3 = 7.6$ (taking $\text{p}K_2$ to be 2.0 as found above). This agrees reasonably with the pH of 7.8 at 3NaOH. $\text{p}K_3$ and $\text{p}K_4$ must be fairly similar, and their average value is about 7.7. The inflection at 4NaOH has a pH of 9.85, making $\text{p}K_5 = 12.0$.

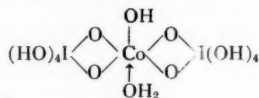
An almost identical titration curve was obtained by adding perchloric acid to a solution

of $\text{Na}_5\text{H}_2\text{Co}(\text{IO}_6)_2$ and titrating the liberated acid with sodium hydroxide; or (in reverse) by titrating $\text{Na}_5\text{H}_2\text{Co}(\text{IO}_6)_2$ with perchloric acid.

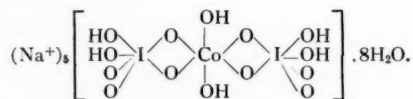
To sum up, pH measurements do not distinguish between the first and second ionization constants of periodatocobaltic acid, or between the third and fourth. The first two hydrogens ionize easily with an average $\text{p}K$ value of 2.0; the next two $\text{p}K$ values average 7.7. The fifth ionization constant is small with $\text{p}K_5 = 12.0$. These values are not very different from those for periodic acid ($\text{p}K_1 = 1.6$, $\text{p}K_2$ about 7). The jump in $\text{p}K$ is very much what is generally found for ionization of successive OH groups attached to a central atom (compare phosphoric acid with successive $\text{p}K$ values of 2.1, 7.2, and 12.3). It is, of course, to be expected that $\text{p}K_1$ and $\text{p}K_2$ should be similar, since this presumably involves ionization of two hydrogens from remote, but identical, parts of the molecule.

(6) General Remarks

It is not yet possible to write a detailed formula for sodium periodatocobaltate (III). There can be little doubt that it contains a complex ion, but it is uncertain whether each periodate is attached by three or two oxygens to the cobalt. Since the co-ordination of cobalt (III) is generally six, in the latter case the other places would have to be taken by water, or OH^- . The acid-base behavior indicates that the two periodate groups are identical in the free acid, and if each periodate is attached by three oxygens it is difficult to write a symmetrical formula. Hence it is perhaps a little more likely that each periodate is attached through two oxygens. This would make the free periodatocobaltic acid:



and the sodium periodatocobaltate (III):



It must be admitted that these formulae are quite speculative; but it is worth noting that the pH behavior can be explained by formulae such as the above, while, if each periodate is attached by three oxygens, it seems impossible to do so.

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SOME PROPERTIES OF SILICA DISPERSIONS¹

A. F. SIRIANNI, F. W. MEADUS, AND I. E. PUDDINGTON

ABSTRACT

When silicic acid sols are formed from solutions of sodium silicate by acid neutralization, a pronounced minimum in the time required for the sol-gel transformation is observed if the titration is stopped near pH 8. If the sol is prepared by electro dialysis, a similar minimum is obtained when the operation is stopped at about pH 5.5. Intermediate values for the minimum are found if the original silicate solution is partially dialyzed followed by neutralization with acid. When the water content of the gels is replaced by liquid hydrocarbons, maximum interaction between the silica particles occurs when the aqua gel has been formed or conditioned at pH 5.5 regardless of the method of preparation of the sol. A minimum in electrophoretic mobility and a maximum in sedimentation rate of the particles are observed at a similar pH value. These properties are modified considerably if the system is thoroughly dehydrated.

INTRODUCTION

A previous investigation (1) of the flow properties of dispersions of finely divided silica in hydrocarbon oils revealed a pronounced and unexpected maximum in the yield value when the silica used had been gelled or conditioned in aqueous solutions of about pH 5 prior to its suspension in oil. Both maximum yield values in suspensions and minimum times for sol-gel transformations might normally be expected to be associated with the maximum degree of interaction between the solid particles of the dispersion. It was surprising, therefore, that the minimum time of set for silica sols, which occurs at about pH 8 when sodium silicate solutions are neutralized with acid (2, 3, 4), did not coincide with the isoelectric point of silicic acid, which is about pH 5 (5). Since minimum gelation times for silica sols prepared by different methods have been variously reported in the pH range 5 to 8 (6), it seemed worth while to re-examine some of the conditions that may influence both this phenomenon and the flow properties of non-aqueous suspensions of the gels.

EXPERIMENTAL

Two types of sodium silicate were used: N grade containing about 28.7% SiO_2 , 8.9% Na_2O , with 62.4% water and Metso Granular containing 28.3% SiO_2 , 29.4% Na_2O , and 42.3% water. Both of these silicates are produced by the Philadelphia Quartz Co. Concentrated solutions were centrifuged to optical clarity prior to dilution to suitable concentrations for experimental purposes.

Substantially cation-free silica sols were prepared by electro dialysis using an American Instrument Co. electro dialyzer fitted with screen platinum electrodes of equal area and a cellophane #600 semipermeable membrane. The cathode compartment of the cell was washed continuously with fresh water to suppress electrolysis owing to a build-up of sodium hydroxide in the compartment. The cathode was positioned about 6 mm from the cellophane membrane to keep the cell resistance as low as possible. Changes in pH in the anode compartment as dialysis proceeded were followed by periodic measurements with a Beckman meter. When the desired pH was reached, the sol in the anode compartment was drained into a clean 600-cc Pyrex beaker prior to shutting off of the current. The beakers containing the sol were sealed with saran wrap.

Sols were also prepared by titrating the sodium silicate solutions to desired pH values with sulphuric acid solution. These sols necessarily contained the sodium sulphate formed during the titration.

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The time of set of the sol was taken as the period between the sol preparation and the time when polymerization and flocculation had proceeded sufficiently for the system to adhere to the sides of the beaker when it was tilted through 45° .

In a number of instances the flow properties of dispersions of particular gels were examined when the water of the aqua gel had been replaced by liquid hydrocarbon. These dispersions were prepared by adding to the mechanically broken gel, after as much water as possible had been removed by vacuum filtration, a mutual solvent for oil and water in an amount slightly in excess of the quantity required to form an azeotrope with the water that remained. The desired quantity of oil was then added and the water and residual solvent removed by evaporation, the final temperature being raised to 125°C for several hours to reduce the free water and solvent content of the system to a minimum. The operation was completed by mechanically homogenizing the system to produce a uniform paste of the silica in the oil. The aqua gels were normally aged for 24 hours prior to displacing their water content with oil. *n*-Propyl alcohol was a satisfactory mutual solvent for oil and water and the final product contained about 5% by weight of silica dispersed in an oil with a viscosity of about 0.6 poise. Viscometric measurements were carried out as previously described (1).

Gels prepared by acid titration were in most instances washed virtually free from salts with distilled water before dispersing them in the oil.

Electrophoretic measurements were conducted on portions of the pastes used for the rheological work diluted with medicinal oil to give a silica concentration of about one per cent. The measurements were carried out as described by Agius and Mulvey (7). The mobility was taken as the plateau in the velocity vs. time curve that appeared within 24 hours after starting the experiment.

Sedimentation experiments were carried out in vertical Pyrex tubes of 20 mm i.d. The suspensions were portions of the samples used in the electrophoretic determinations.

RESULTS AND DISCUSSION

Typical data relating gelation time for dialyzed sodium silicate and the pH of the sol are shown in Fig. 1. A pronounced minimum occurred at about pH 5.5, and this was substantially independent of the type of sodium silicate used, the concentration range explored, or the source of the water used in washing the cathode compartment of the cell. Softer gels with no odor of chlorine and gelation times up to 500 times longer were obtained when conductivity water was substituted for tap water in the washing procedure. The minimum time of set increased from 9 to 22 hours when the silica concentration was reduced from 4.15 to 2.92% and conductivity water was used to wash the cathode compartment. With a tap water wash the minimum time of set for a sol containing 3.6% SiO_2 was 4 minutes. These observations are consistent with those of Hurd and co-workers (8) on the effect of impurities and solids concentration on the time of set.

Since the behavior of a series of gels prepared by titration of sodium silicate solutions with sulphuric acid agreed with the results of previous investigations in that the minimum gelation time was about 4 seconds at a pH of 7.9 for a sol containing 3.6% SiO_2 , it is apparent that the difference in the pH for minimum gelation time for these sols is owing to the presence of electrolytes from the reagents used in their preparation. It is quite possible, however, that the ions from different acids could modify the magnitude of the effect.

Two further series of gels prepared by partial electrodialysis, followed by titration with sulphuric acid to the desired end points, showed that the pH of minimum gelation time decreased regularly as the amount of electrolyte in the final sol was reduced.

The flow properties of 5% by weight dispersions of silica in hydrocarbon oil are

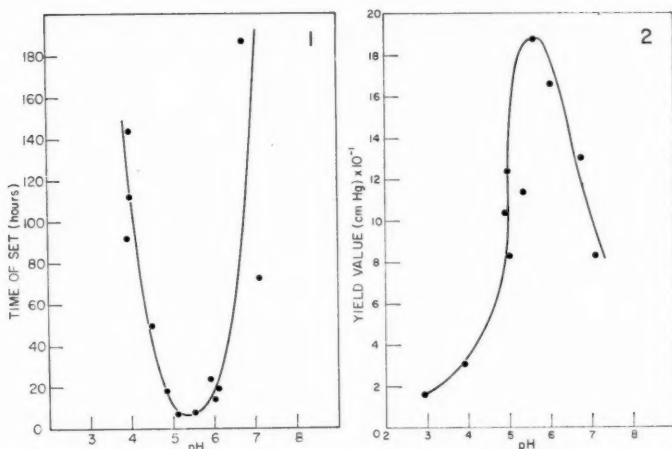


FIG. 1. Dependence of gelation times for dialyzed sodium silicate solutions on the pH of the sol.

FIG. 2. Yield values of 5% dispersions of silica in hydrocarbon oils as a function of the pH at which the silica was prepared.

indicated in Fig. 2. This shows the change in yield value of the dispersion as a function of the pH at which the sol-gel transformation occurred. A very pronounced maximum in the yield value was found at about pH 5.5 and this was independent of the method of gel preparation. Since the yield value of the pastes and the setting of gels both indicate interaction between the solid particles forming the structure, it seems that the behavior of silica in oil and in aqueous media is rather similar. The yield value of the silica-oil pastes was modified only slightly by the presence of sodium sulphate, and comparable flow properties were found when the gels were prepared by dialysis and by acid precipitation with or without the removal of the sodium sulphate. On the other hand, the aqua gels were considerably softer when prepared by dialysis using a conductivity water wash of the cathode cell and it would appear that electrolytes exert a strong flocculating influence on the polymerized silicic acid. Their inertness in oil is probably owing to their almost complete insolubility in that medium. A maximum in the elastic properties has also been observed for silica gels prepared near the point of minimum gelation time when the sols were formed by acid neutralization (9). This, too, is indicative of a high degree of adhesion between the flocculated particles.

The sedimentation rates and electrophoretic mobility of silica dispersed in oil are shown in Fig. 3. The maximum sedimentation rate which occurs at the same pH value as the maximum yield value in the more concentrated pastes strongly suggests a high degree of flocculation, and this, in turn, is indicative of higher particle interaction at this point. That the improved stability of the sols containing silica prepared above and below pH 5.5 is probably electrical in origin is suggested by the electrophoretic behavior. The mobility is essentially zero at the pH of maximum particle interaction in an electric field of about 70 v per cm with a velocity of migration rising sharply on either side of this minimum. The direction of particle motion indicates opposite charge on the silica on either side of the minimum and this is supported by the fact that the mixtures prepared from equal quantities of positively and negatively charged sols showed flocculation properties similar to those of the neutral sols. However, since some agitation is necessary to prepare the suspensions, and the oil has a very high electrical resistance, the possibility of the charges

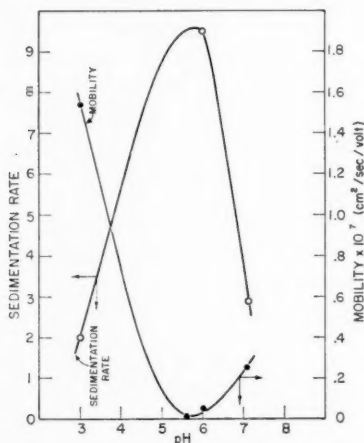


FIG. 3. Sedimentation rates and electrophoretic mobilities of finely divided silica prepared at different pH values in liquid hydrocarbons.

arising from the relative motion of the solid and the liquid cannot be ruled out completely. In those systems showing the highest mobilities there was a tendency for the velocity of migration to decrease after about 40 hours in the electrophoretic cell. No corresponding change in the sedimentation velocity of the more stable suspensions was observed, however, and the adsorption of oil-soluble ionic substances such as traces of hydrocarbon oxidation products is perhaps a more reasonable explanation for the apparent particle charge.

Although the amounts of water in these preparations must be small, traces of water have been observed to exert an influence on the electrical properties of non-aqueous systems (10), and the amounts desorbed from container walls may be important. To assess this point, the suspensions used in the sedimentation and in the electrophoretic work were diluted in their containers with 10% of toluene, which was then removed by boiling off at atmospheric pressure. This treatment had the general effect of making the sedimentation and electrical properties more uniform and similar in magnitude to those at the isoelectric point. It would thus appear that traces of water may exert an appreciable influence on the electrical properties of non-aqueous suspensions probably because of the enhanced ionizing power of the organic liquid containing it. No significant changes in the flow properties of more concentrated suspensions could be observed, however, after a similar treatment. The increased particle interaction is thus not sufficient to have an appreciable effect on the yield value.

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THE RELATIVE ENTHALPIES OF CONCENTRATED POTASSIUM HYDROXIDE SOLUTIONS¹

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ABSTRACT

Measurements were made of the heats of neutralization of concentrated solutions of potassium hydroxide with hydrochloric acid, with an estimated accuracy better than one part per thousand. From this information it was possible to calculate relative enthalpy data for potassium hydroxide solutions up to 16 molal.

INTRODUCTION

The relative enthalpies of potassium hydroxide solutions have been measured calorimetrically in the relatively dilute range by Richards and Rowe (1), and over an extended concentration range by Bender and Akerlof (2), using an electromotive force method similar to the work of Akerlof and Kegeles (3) with sodium hydroxide solutions, and presumably of comparable accuracy. Because, as aptly pointed out by Harned and Owen (4), electromotive force data must be regarded as hypothetical until substantiated by other evidence, it appeared desirable to verify these high concentration values by calorimetric measurement.

As has been previously established (5, 6), heat of neutralization measurements can supply data from which relative enthalpy values can be derived conveniently and reliably, provided necessary auxiliary data are available. Because of the availability of both suitable equipment and the prerequisite data, the heats of neutralization of potassium hydroxide solutions by hydrochloric acid solutions were measured over a wide concentration range. This information was utilized in the computation of the relative enthalpies of potassium hydroxide solutions over a concentration range of 3 to 16 molal.

EXPERIMENTAL AND RESULTS

The calorimetric equipment and general method of operation have been described previously (5, 7). Reagent grade potassium hydroxide was freed of carbonate by standard procedures, and reagent grade hydrochloric acid was used without further treatment. Stock solutions were diluted as required with conductivity water and the diluted solutions analyzed gravimetrically by the precipitation of an equivalent amount of silver chloride.

The heat liberated in the bomb reaction differs from the desired quantity, the heat of neutralization of potassium hydroxide solution by hydrochloric acid solution, both at the same molal concentration m and 25.00° C, because of simultaneous heat effects, the most important being caused by:

- (1) The solution of hydrogen chloride from the vapor phase after completion of the reaction.
- (2) Dilution effects due to the impracticability of adjusting the concentrations of the reactants to exactly the same molality.
- (3) A slight excess of one reactant being experimentally unavoidable; hydrochloric acid was therefore added in slight excess, thus minimizing the error due to any residual carbonate in the base. An enthalpy change is involved in the dilution of this excess acid.

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Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Canada.

TABLE I

Heats of neutralization of potassium hydroxide solutions by hydrochloric acid as observed experimentally

Reactant concentration (moles solute/kg solvent)	Observed heat of neutralization (defined calories at 25.00° C)	Reactant concentration (moles solute/kg solvent)	Observed heat of neutralization (defined calories at 25.00° C)
15.985	-21,448	10.126	-17,693
	21,437		17,692
14.961	20,838	9.034	17,213
14.915	20,816		17,194
	20,817		17,186
12.960	15,593	7.000	16,255
	15,596		16,257
12.023	18,963	6.987	16,251
	18,965		16,260
11.005	18,195	4.990	15,383
	18,212		15,378
10.969	18,181	3.113	14,605
	18,177		14,616

(4) A reaction temperature other than 25.00° C, except in the fortuitous case of the calorimeter being exactly 25.00° C when the reaction is initiated.

The heats of neutralization reported in Table I have been computed from the heats of the bomb reactions by "correcting" them for the above-mentioned heat effects. Experimental conditions were carefully controlled so that these corrections were small and the uncertainties involved in their calculation are negligible compared to experimental errors. Smoothed values of the heats of neutralization at integral values of the concentration are shown in Table II.

TABLE II

Smoothed values of the heats of neutralization of potassium hydroxide by hydrochloric acid

Molality	Heat of neutralization (defined calories)	Molality	Heat of neutralization (defined calories)	Molality	Heat of neutralization (defined calories)
3	-14,560	8	-16,715	12	-18,945
4	14,965	9	17,185	13	19,620
5	15,390	10	17,635	14	20,255
6	15,815	10.56	17,885	15	20,865
7	16,260	11	18,200	16	21,450

The only auxiliary data whose reliability could significantly affect the accuracy of the heats of neutralization are the specific heats of the product solutions, which were used in computing the heat capacity of the system. Values of the specific heats of potassium chloride solutions over the pertinent concentration range are available from Randall and Bison (8), Bousfield and Bousfield (9), and Galagoleva-Cherbou (10). When compared graphically, the average deviation of the experiment points was less than 0.1% from the mean curve, an insignificant error with respect to the use.

Calculation of the relative enthalpies of potassium hydroxide solutions from the smoothed heat of neutralization data involves the use of the relationship:

$$\Delta H_N = \Delta H_N^\circ + [L_2(\text{KCl})_{m'} - L_2(\text{KOH})_m - L_2(\text{HCl})_m] + (55.51/m) \times [(m/m') L_1(\text{KCl})_{m'} - L_1(\text{KOH})_m - L_1(\text{HCl})_m]$$

at concentrations below the saturation concentration of potassium chloride. When the solubility of potassium chloride is exceeded, the enthalpy relationship takes the form:

$$\Delta H_N = \Delta H_N^\circ + [L_2(\text{KCl})_{\text{sat}} - L_2(\text{KOH})_m - L_2(\text{HCl})_m] + \{(1 - m_{\text{sat}})/m'\} \\ \times [H_{\text{solid}} - H_2(\text{KCl})_{\text{sat}}] + (55.51/m) [m/m' L_1(\text{KCl})_{\text{sat}} - L_1(\text{KOH})_m - L_1(\text{HCl})_m]$$

where " m " is used to designate the molality of the reactants, m' is used for $(55.51 m)/(111.02 + m)$, and m_{sat} is used to indicate the molality of saturated potassium chloride solution, 10.56 moles per kilogram of solvent. ΔH_N refers to the heat of neutralization at a reactant molality m , and ΔH_N° the heat of neutralization at infinite dilution. Supplementary data used were: heat of dilution data for potassium chloride solutions from Lange *et al.* (11), relative enthalpy data for hydrochloric acid solutions from Akerlof and Teare (12) and Sturtevant (13), and the heat of neutralization at infinite dilution was taken as -13.32 defined kilocalories (7). Differential heat of solution of potassium chloride was taken from Wüst and Lange (14); as macrocrystalline potassium chloride was produced in the present work, their initial and final states correspond to those encountered here.

Table III contains the relative partial molal enthalpies of solvent and solute, and the relative enthalpies per mole of solute for potassium hydroxide solutions at integral values of the solute concentration over the range 3 to 16 molal, calculated as described above.

TABLE III
Relative enthalpies of potassium hydroxide solution, defined kilocalories at 25.00° C

m	L_1	L_2	L	m	L_1	L_2	L
3	-.018	+.63	+.30	10	-.370	+3.43	+1.38
4	.035	.91	.42	11	.475	4.02	1.57
5	.061	1.24	.56	12	.612	4.67	1.84
6	.098	1.59	.69	13	.690	5.01	2.07
7	.146	2.00	.84	14	.771	5.36	2.29
8	.206	2.45	1.02	15	.855	5.67	2.51
9	.280	2.93	1.20	16	.942	5.98	2.71

DISCUSSION

Analysis of the results and a consideration of the contributing sources of error lead to the conclusion that the heat of neutralization values obtained are uncertain to less than 0.1%.

Further confidence in the reliability of the heat of neutralization data is obtained from a study of the discontinuity in the heat of neutralization versus concentration curve. At a reactant concentration of 10.56 molal, a discontinuity appears due to the precipitation of potassium chloride. The experimentally determined upper and lower sections of the curve fall within 5 calories of each other when extended to this point, and the change of slope is 283 units, compared with the calculated value of 270 units.

The average deviation between these relative molar enthalpies and those reported by Akerlof and Bender is about 100 calories, which is similar to the discrepancy between the Akerlof and Kegeles values and the calorimetric values of Bertetti and McCabe (16) for sodium hydroxide solutions.

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A DETAILED STUDY OF THE SAMUEL-MAGEE MODEL FOR THE RADIATION CHEMISTRY OF WATER

PART II. KINETICS OF RADICAL REACTIONS IN THE TRACKS OF DENSELY IONIZING PARTICLES¹

P. J. DYNE AND J. M. KENNEDY

ABSTRACT

The kinetics of recombination of H and OH radicals, formed in liquid water along the track of a densely ionizing particle in the manner suggested by Samuel and Magee, have been studied using an electronic computer. The variation in yields with track density is in good qualitative agreement with experiment. Arguments are advanced to show that the energy required to produce one effective radical pair in liquid water is about 20 ev. Discussions are presented of the effects of scavenger concentration and its depletion at the center of the track, track diameter, the value of the rate constant for the recombination of H atoms and OH radicals, and the value of $G(-H_2O)$ as a function of track density.

1. INTRODUCTION

This paper presents calculations performed on the Chalk River Datatron Computer on the kinetics of diffusion and recombination of H and OH radicals formed in water along the track of a densely ionizing particle, such as a proton or an α -particle. According to the model suggested by Samuel and Magee (1) these radicals are formed by the dissociation of excited water molecules which, in turn, result from the ionization and excitation brought about by the ionizing particle. These radicals have similar spatial distributions, lying in a uniform column along the track of the particle. The concentration of these radicals falls off rapidly across the axis of the column according to a Gaussian or some similar distribution. The diffusion processes are, accordingly, described in a cylindrical co-ordinate system.

In the tracks of lightly ionizing particles (fast electrons) the excitation is localized into small clusters or spurs containing a few (four to eight) radical pairs. These spurs have spherical symmetry and the diffusion process is described in a spherical co-ordinate system. In a previous paper (2), which will be referred to as Part I or (I), we presented calculations of the kinetics of recombination of H and OH radicals in these small spurs. The present paper is an extension of the techniques and arguments used in Part I to cylindrical tracks. The reader is referred to Sections 1 and 2 of Part I for a more detailed introduction to the topic.

2. THE TRACK EQUATION

We adopt the convention that the hydrogen atom is species 1, with diffusion constant D_1 , recombination rate constant k_{11} , and concentration C_1 , which is a function of time and space. The OH radical is species 2 with constants D_2 , k_{22} , C_2 , etc. The rate constant for recombination of H and OH radicals is k_{12} . The radical scavenger is species 3, with diffusion constant D_3 ; the rate constants for reaction of scavenger with radicals 1, 2 are k_{13} , k_{23} respectively.

The track equations governing the kinetics of reaction and diffusion are:

$$\begin{aligned} [1] \quad & \partial C_1 / \partial t = D_1 \nabla^2 C_1 - 2k_{11} C_1^2 - k_{12} C_1 C_2 - k_{13} C_1 C_3 \\ [2] \quad & \partial C_2 / \partial t = D_2 \nabla^2 C_2 - 2k_{22} C_2^2 - k_{12} C_1 C_2 - k_{23} C_2 C_3 \\ [3] \quad & \partial C_3 / \partial t = D_3 \nabla^2 C_3 - k_{13} C_1 C_3 - k_{23} C_2 C_3. \end{aligned}$$

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These equations differ from those used for γ -ray spurs in three respects.

(a) The Laplacian refers to cylindrical, not spherical co-ordinates.

(b) There is no weighting function in front of the terms $k_{11}C_1^2$ and $k_{22}C_2^2$. In a γ -ray spur containing, say, five radicals, the bimolecular rate is given by $4/5 k_{11}C_1^2$, since one radical can only react with four others. The cylindrical tracks are long and so N , the number of radicals in the track, is large and the weighting function $(N-1)/N$ is not significantly different from unity.

(c) The introduction of equation [3], which describes the depletion of scavenger at the center of the track and its replacement by diffusion from the bulk of the liquid.

The yields of hydrogen and hydrogen peroxide are the values of

$$\int_0^\infty \int_0^\infty k_{11}C_1^2 dv \cdot dt \quad \text{and} \quad \int_0^\infty \int_0^\infty k_{22}C_2^2 dv \cdot dt,$$

respectively, while

$$\int_0^\infty \int_0^\infty k_{12}C_1C_2 dv \cdot dt$$

is the amount of H_2O re-formed in the track. The numerical method is described in the Appendix.

3. THE CHOICE OF CONSTANTS

Rate constants and diffusion constants are chosen essentially as in Part I. They are $D_2 = 2 \times 10^{-5}$ cm²/sec, $D_1 = 8 \times 10^{-5}$ cm²/sec, $k_{11} = 6.0 \times 10^{-12}$, $k_{12} = 15 \times 10^{-12}$, $k_{22} = 4.5 \times 10^{-12}$ cc/molecule sec.² Constants k_{13} were taken as 1.0×10^{-11} cc/molecule sec, D_3 was taken as 2×10^{-5} cm²/sec. If it is assumed that the radicals have a Gaussian distribution, the track radius is expressed by the parameters β_1, β_2 where $C_1(r) = (N_1\beta_1^2/\pi) \exp(-\beta_1^2 r^2)$. N_1 is the number of radicals/ \AA . For initial studies we have taken $1/\beta = 10^{-7}$ cm = 10 \AA for species 1 and 2. In the following discussion it is, at times, more illustrative to use the parameter $R = 1/\beta$, which can be visualized as the "radius" of the track. The "concentration" of scavenger in the initial calculation is $10^{-3} M$ (6.0×10^{17} molecules/cc). As experimental rate constants of scavengers are nearer 10^{-10} cc/molecule sec rather than the value of 10^{-11} which we use in the calculation, the equivalent experimental concentration of scavenger is nearer $10^{-4} M$.

The track density is expressed by the parameters N_1 and N_2 , the number of radicals/ \AA . Cases were examined over the range 0.1–10 radicals/ \AA . We have converted the number of radicals/ \AA to L.E.T. (Linear Energy Transfer) (ev/ \AA) using the arbitrary figure of an energy deposition of 10 ev to give one radical pair. This value is derived from Firestone's measurement of $G(-H_2O) = 11 \pm 1$ (3) for the decomposition of water vapor (Part I, Section 4). If, for instance, $N_1 = N_2 = 0.2$ radicals/ \AA then this corresponds to a particle track with an L.E.T. of 2 ev/ \AA . Our L.E.T. values should not be used too literally because, as will be shown in subsequent discussion, the value of 10 ev/radical pair is a minimum value. The effective value in liquid water may be nearer 20 ev/radical pair.

²The rate constants k_{11}, k_{22} were defined in an inconsistent manner in Part I. The value of k_{11} , for instance, in the normal chemical definition gives the number of reactions $H + H \rightarrow H_2$. The value of k_{11} used in the program was used to calculate the number of hydrogen atoms removed by recombination and is therefore a factor of 2 greater than the rate constant defined "chemically". The rate constants k_{11} and k_{22} tabulated in Table I of Part I are just twice the "chemical rate constants" for each case, e.g. the initial case "A" has "true" chemical rate constants, $k_{11} = 6 \times 10^{-12}$, $k_{22} = 4.5 \times 10^{-12}$, $k_{12} = 30 \times 10^{-12}$. This differs essentially from the initial case defined in Part II in that k_{12} is larger by a factor of two. This error in definition does not affect the results and conclusions of Part I.

4. THE CALCULATIONS

The detailed results of the calculations are presented in Table I. The numbers to the left of the double line are the constants which specify the individual case: those to the right are the yields of molecular products and scavenged radicals. These are expressed as fractions of one initial radical pair. The yields of H_2 and H_2O_2 are expressed as the number of atoms or radicals which have recombined to give these molecular products. The numbers of molecules, H_2 and H_2O_2 , formed are half these numbers. The number of water molecules re-formed is $[H_2O^*]$, the net decomposition of H_2O is $[-H_2O]$. The yields defined in this manner, symbolized by enclosure in square brackets, obey these stoichiometric relationships:

$$[\text{H}_2] + [\text{H}_2\text{O}^*] + [\text{H}] = [\text{H}_2\text{O}_2] + [\text{H}_2\text{O}^*] + [\text{OH}] = [\text{H}_2\text{O}^*] + [-\text{H}_2\text{O}] = 1.$$

(The yields for γ -ray spurs in Part I were expressed as the number of radicals, etc., per spur. They are identical with the yields defined above when divided by the number of radical pairs/spur.)

The final yields at infinite time are estimated numerically as follows. If the number of radicals recombined at times t_A and t_B are N_A and N_B ($t_B > t_A$) then the number of radicals recombined at infinite time is $N_\infty = N_B + 9.5(N_B - N_A)$. This formula is justified in the Appendix. The yields of radicals which escape recombination are small and obtained by difference between two larger numbers, e.g. $[\text{OH}] = [-\text{H}_2\text{O}] - [\text{H}_2\text{O}_2]$. Small errors in estimating the molecular yields make larger errors in the radical yields. The radical yields, particularly at high L.E.T., have consequently rather low numerical precision.

The results of a typical calculation are shown in Fig. 1. The features of interest are firstly, the time scale during which significant reaction takes place—four orders of magnitude are plotted—and secondly, the large amount of total recombination which occurs in 10^{-9} seconds as compared with the extent of recombination in γ -ray spurs (Fig. 1, Part I). The effects of diffusion control are shown by the crossing of the curves for $[H_2]$ and $[H_2O_2]$. Initially $[H_2]$ is greater than $[H_2O_2]$ because $k_{11} > k_{22}$. After 10^{-10} seconds, however, hydrogen atoms have been removed from the center of the track so that $k_{11}[H]^2$ is less than $k_{22}[OH]^2$, and the yield of H_2O_2 becomes greater than that of H_2 .

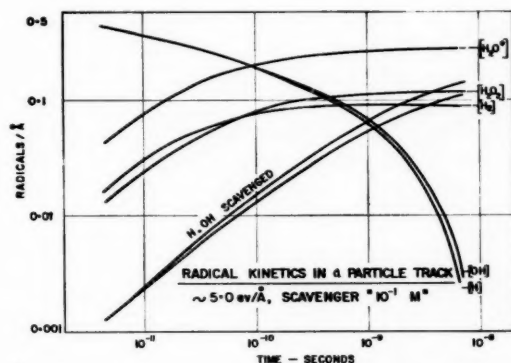


FIG. 1. Kinetics of recombination in a cylindrical track for case I.

TABLE I
Computed molecular and radical yields for cylindrical tracks

Case	$k_{11} \times 10^{12}$	$k_{12} \times 10^{12}$	$k_{13} \times 10^{12}$	$k_{12} \times 10^{12}$	$k_{13} \times 10^{12}$	$D_1 \times 10^5$	$D_2 \times 10^5$	$D_3 \times 10^5$	$N_1 = N_2 \times 10^{-7}$	$\beta_1 \times 10^{-7}$	$\beta_2 \times 10^{-7}$	$C_3 \pm 6 \times 10^{17}$	[H ₂]	[H ₂ O ₂]	[H ₂ O [•]]	[H]	[OH]	[•H ₂ O]
A } Variation of track density	6.0	4.5	15.0	10.0	8.0	2.0	2.0	2.0	0.1	1.0	1.0	1.0	0.208	0.370	0.338	0.454	0.292	0.662
B	"	"	"	"	"	"	"	"	0.2	"	"	"	0.272	0.412	0.418	0.307	0.168	0.580
C	"	"	"	"	"	"	"	"	0.5	"	"	"	0.338	0.438	0.494	0.168	0.068	0.506
D	"	"	"	"	"	"	"	"	1.0	"	"	"	0.371	0.438	0.531	0.068	0.031	0.469
E	"	"	"	"	"	"	"	"	2.0	"	"	"	0.391	0.427	0.530	0.069	0.023	0.480
F	"	"	"	"	"	"	"	"	10.0	"	"	"	0.408	0.418	0.578	0.013	0.004	0.422
G } Variation of scavenger concentration	6.0	4.5	30.0	"	"	"	"	"	0.5	"	"	1	0.224	0.290	0.651	0.122	0.056	0.346
H	"	"	"	"	"	"	"	"	"	"	"	10	0.214	0.279	0.634	0.152	0.087	0.369
I	"	"	"	"	"	"	"	"	"	"	"	10 ²	0.185	0.237	0.554	0.202	0.210	0.446
J	"	"	"	"	"	"	"	"	"	"	"	10 ³	0.134	0.150	0.390	0.476	0.460	0.610
K	"	"	"	10 ⁻²	"	"	"	"	"	"	"	10 ⁴	0.128	0.138	0.370	0.502	0.492	0.630
L	"	"	"	10.0	"	"	"	0.5	"	"	"	10 ⁵	0.132	0.151	0.391	0.476	0.456	0.608
M } Varying k_{12}	"	"	10	"	"	"	"	2.0	"	"	"	1.0	0.408	0.522	0.368	0.206	0.092	0.614
N	"	"	3.0	"	"	"	"	"	"	"	"	"	0.576	0.724	0.166	0.258	0.110	0.834
O	"	"	90	"	"	"	"	"	"	"	"	"	0.098	0.123	0.890	0.030	0.026	0.149
P } Varying spur diameter	"	"	30.0	"	"	"	"	"	"	0.5	0.5	"	0.220	0.288	0.650	0.130	0.062	0.350
Q	"	"	"	"	"	"	"	"	"	1.0	1.0	"	0.224	0.290	0.651	0.122	0.056	0.346
R	"	"	"	"	"	"	"	"	"	2.0	2.0	"	0.224	0.294	0.660	0.116	0.046	0.340
S } Varying β_1	"	"	"	"	"	"	"	"	"	0.65	1.0	"	0.228	0.344	0.620	0.152	0.036	0.380
T	"	"	"	"	"	"	"	"	"	0.4	"	"	0.258	0.434	0.538	0.204	0.028	0.462

NOTE: The columns to the left of the double line refer to the parameters of the track and are explained in Sections 3 and 4. The columns to the right of the double line give the computed yields defined in Section 4.

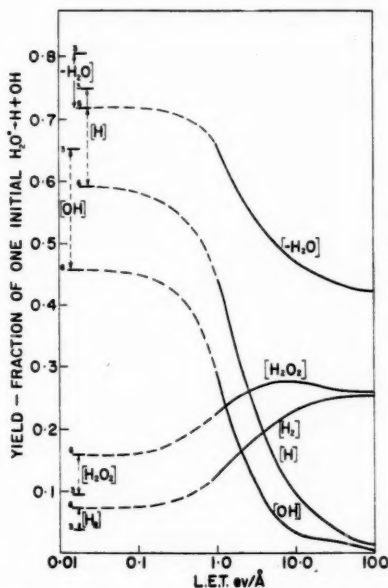


FIG. 2. Variation in yields with track density. The solid lines at the right of the figure are obtained from cases A-F. The yields at the left of the figure, plotted at L.E.T. of 0.02 ev/Å are for spherical spurs with three or six radical pairs/spur. The dotted lines are interpolations; no calculations have been made in this region. The scale of L.E.T. is arbitrary and can only be compared qualitatively with Fig. 3. For further details see text.

5. VARIATION IN YIELDS WITH TRACK DENSITY

The variation in yield with track density is shown in Fig. 2. The solid curves cover the range 0.1–10 radical pairs/Å and are derived from cases A-F (Table I). These cases use the rate constants, diffusion constants, and other parameters chosen for the "initial case" in the previous section. Note again that the scale of linear energy transfer in ev/Å is obtained from the track density using the arbitrary value of 10 ev/radical pair. Yields for γ -ray spurs for the same choice of rate constants and diffusion constants are plotted at a value of 0.02 ev/Å (corresponding to Compton recoils generated by ~ 1 -Mev γ -rays). Values for both three and six radical pairs/spur are shown.

The yields are expressed as the number of molecules or radicals formed per initial H_2O dissociated. These are identical with the figures given in Table I except that the values of $[\text{H}_2]$ and $[\text{H}_2\text{O}_2]$ are divided by two. The yields as plotted are proportional to G -values (molecules/100 ev). The dotted portions of the curves in Fig. 2 lie in the region where the track expands partly in spherical and partly in cylindrical geometry. The present calculations do not cover this range and the curves have been drawn on the assumption that there is an asymptotic approach of the yields to the values for isolated spurs.

The calculations have been carried over the extreme range for which the cylindrical approximation is valid; at a track density as low as 0.1 radicals/Å and with a value of 10 Å for the modulus of the Gaussian, the track may be more correctly visualized as a series of spherical spurs which are just overlapping or touching. The errors involved are probably small because of the short time which elapses before such a track expands to a

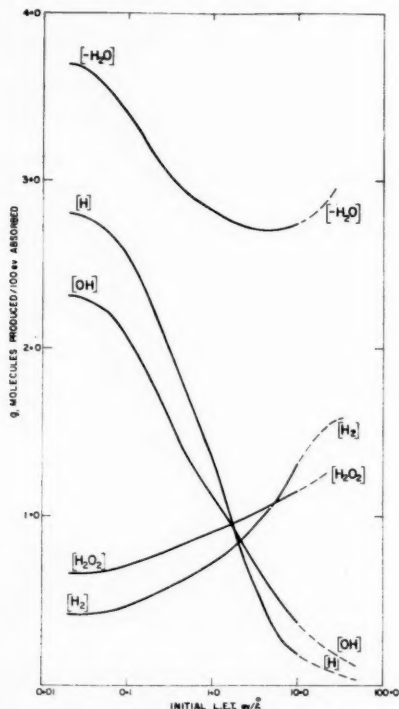


FIG. 3. Experimental variation in yields with initial track density. The figure shows smoothed, idealized curves based largely on the data of Schwarz, Caffrey, and Scholes.

uniform cylinder and because of the relative insensitivity of the yield to the initial track diameter. The errors will be in the direction of underestimating the amount of recombination.

Figure 2 is qualitatively in good agreement with experiment and may be compared with Fig. 3, which presents the experimental data for pure water in a somewhat idealized fashion. Figure 2 should also be compared with Figs. 2-16, reference 13, which present similar curves for acid solutions. The experimental curves are similar and differ mainly in numerical details.

Both in theory and experiment the yields of radicals decrease and the molecular yields increase with increasing L.E.T. In very dense tracks the radical yields are virtually zero. At the same time the ratio of the molecular yields $[H_2O_2]/[H_2]$ decreases. At low L.E.T. $[H_2O_2] > [H_2]$ but at high L.E.T. they approach equality. In the calculation the inequality arises because of the greater diffusion constant chosen for hydrogen atoms; this removes hydrogen atoms more rapidly from the high-density region of the track where the bulk of bimolecular recombination takes place. In the highest-density cylindrical tracks the effects of diffusion are reduced and the yields are not very different from those predicted by homogeneous kinetics.

The small maximum in the calculated value of $[H_2O_2]$ is another consequence of the more rapid diffusion of hydrogen atoms. The studies in Part I showed that $[H_2O_2]$ was strongly influenced by the availability of hydrogen atoms which compete for OH radicals

by the $\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$ recombination. The maximum in $[\text{H}_2\text{O}_2]$ occurs where the diffusion of H atoms is becoming significant, their removal from the center of the track increases the availability of OH for recombination to H_2O_2 , and consequently $[\text{H}_2\text{O}_2]$ shows a slight maximum. The effect is quite small and would be difficult to observe experimentally. The calculated maximum is only significant in illustrating the kinetic complexities of the system and the somewhat unexpected effects of competing processes.

It is possible that the experimentally observed increase in $G(\text{H}_2)$ at high L.E.T. (see Fig. 3 and ref. 4) making $G(\text{H}_2) > G(\text{H}_2\text{O}_2)$ could be the result of similar kinetic effects if k_{11} were made much larger than the values chosen here. A few calculations (not specified in Table I) showed, however, that the changes in the constants required to produce such an effect were too drastic to be reasonable.

(a) *The Energy Scale*

The calculated value of $[-\text{H}_2\text{O}]$ varies from ~ 0.8 for a γ -ray spur containing initially three radical pairs to ~ 0.5 for a track having 0.5 radical pairs/ \AA . Combining these figures with the value of ~ 10 ev/initial radical pair we find $G(-\text{H}_2\text{O})$ (molecules/100 ev) to be ~ 8 for γ -rays and ~ 5 for a particle track with L.E.T. of 5 ev/ \AA . These values are greater, by a factor ~ 2 , than the experimental values. $G(-\text{H}_2\text{O})$ for γ -rays in neutral water is 3.7 (2). For 11-Mev α -particles in neutral water $G(-\text{H}_2\text{O})$ is 2.57 (4). The energy required to produce one radical pair must be ~ 20 ev/radical pair (essentially double our initial estimate) to give agreement with experiment.

The same conclusion has been reached by both Schwarz, Caffrey, and Scholes (4) and Burton and Kurien (5). Both these groups of workers estimated *initial* values of $G(-\text{H}_2\text{O})$, designated G^0 , from experimentally determined values of $G(-\text{H}_2\text{O})$, $G(\text{H}_2)$, and $G(\text{H}_2\text{O}_2)$. This was done by putting

$$G(\text{H}_2\text{O}^*) = G(\text{H}_2) + G(\text{H}_2\text{O}_2). \quad [4]$$

$G(\text{H}_2\text{O}^*)$ is the yield of water re-formed in the track and is equivalent to $[\text{H}_2\text{O}^*]$ in our terminology.³ The values of G^0 are obtained by putting

$$G^0 = G(-\text{H}_2\text{O}) + G(\text{H}_2\text{O}^*).$$

The assumption of equation [4] is equivalent, in these calculations, to putting $k_{11} = k_{12} = k_{22}$ and $D_1 = D_2$. The constants used in this paper would make $G(\text{H}_2\text{O}^*) \simeq 1.3(G(\text{H}_2) + G(\text{H}_2\text{O}_2))$ so that the approximation is not unreasonable. With these assumptions Schwarz *et al.* found $G^0 = 4.4$ – 4.7 in neutral solution for Co-60 γ -rays increasing to 6.1 for 3.5-Mev α 's. In acid solution Burton and Kurien found $G^0 = 6.3$ – 6.7 for Co-60 γ -rays and 50-kev X-rays, and $G^0 = 7.3$ for α -rays with an average energy of 3.4 Mev.

The constancy of G^0 -values over a fair energy range in both series of experiments supports the validity of the calculation. A value of $G^0 \simeq 5$ corresponds again to an energy requirement of ~ 20 ev/radical pair. It follows, therefore, that the value of ~ 10 ev/radical pair, obtained experimentally by Firestone (3) from studies in water vapor, is not directly applicable to liquid water.

The gas-phase and liquid values of the initial radical yield may be reconciled if it is assumed that there is a very high initial probability of an H, OH pair recombining in the first few diffusion steps. The effective radical pair yield is then less than the instantaneous initial value (4).

³Burton and Kurien use a modified relation $G(\text{H}_2\text{O}^*) = (N-1)/N (G(\text{H}_2) + G(\text{H}_2\text{O}_2))$ for γ -ray spurs where N is the number of radical pairs/spur.

(b) *The Variation of $G(-H_2O)$ with L.E.T.*

The value of $[-H_2O]$ falls with increasing L.E.T. as do the experimental values of $G(-H_2O)$ in pure water. The experimental ratio $G(-H_2O)$ γ -rays/ $G(-H_2O)$ 11.5-Mev α -rays is 1.4 (4). The calculated ratio using the "initial" rate constants and diffusion constants for a track with 0.5 radicals/ \AA is 1.4 if the γ -ray spur contains six radical pairs and 1.6 if the spur contains three radical pairs. This we regard as being in qualitative agreement with experiment. The values obtained in acid solution are in less satisfactory agreement. Burton and Kurien (5) report a value of 1.12 for the ratio of $G(-H_2O)$ γ -rays/ $G(-H_2O)$ 5.3-Mev α -rays in 0.8 N H_2SO_4 ; significantly different from the values in neutral water and from our quoted calculations.

The calculated value of this ratio is, however, a sensitive function of the value chosen for k_{12} . A plot of the ratio of $[-H_2O]$ for a γ -ray spur containing six radical pairs to $[-H_2O]$ for cylindrical tracks with $N_1 = N_2 = 0.5$ radical pairs/ \AA , is shown in Fig. 4. A value of 1.1 for this ratio is obtained with $k_{12} = 0.5 \times 10^{-11}$, 1/8 of the value chosen in the initial series of calculations. This figure is derived from cases M, N, and O and some calculations on γ -ray spurs not published in Part I.

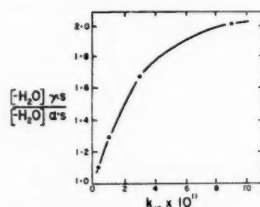


FIG. 4. The variation in $[-H_2O]$ as a function of k_{12} , expressed as the ratio $[-H_2O]$ γ 's/ $[-H_2O]$ α 's for spherical spurs with six radical pairs/spur and cylindrical tracks with $N_1 = N_2 = 0.5/\text{\AA}$.

The kinetic scheme used here to describe the Samuel-Magee model does, therefore, predict a reduction in $[-H_2O]$ in pure water with increasing L.E.T. which is qualitatively in agreement with experiment. The change in this and other yields with pH shows, however, that this kinetic scheme is incomplete. The observed pH effects may, *inter alia*, be equivalent to processes which, in effect, change the value of k_{12} in the simple kinetic scheme.

An increase in $G(-H_2O)$ at high L.E.T. has been observed by several workers. This has been qualitatively explained by Schwarz, Caffrey, and Scholes (4). It is supposed that the H and OH radicals from the dissociation of 1 water molecule are initially so close together that there is a fairly high probability of these two radicals recombining. At very high ionization densities however, the density of excited water molecules, and hence of H and OH radicals, is so high that one hydrogen atom is more likely to recombine with another hydrogen atom than to recombine with the OH from which it was dissociated. If this competing reaction for formation of H_2O_2 and H_2 is at all favorable then $G(-H_2O)$ will increase at high track densities.⁴ This process could also explain the difference between the initial radical yields in the gas and liquid phases; in the gas phase the recombination of H and OH formed from 1 individual water molecule would

⁴This explanation neglects the opposite effect where H atoms are closer to OH radicals produced from neighboring excited water molecules. This effect would decrease $G(-H_2O)$ as the track density increases and could exactly counterbalance the effect described above. This comment underlines the complexity of radical correlation effects.

be less probable. Effects of this nature could be formally incorporated into the kinetic scheme of the model by the introduction of time-dependent rate constants. A procedure for doing this has been advanced by Monchick, Samuel, and Magee (11).

6. THE EFFECT OF SCAVENGER CONCENTRATION

The reduction in yields of molecular products as the concentration of scavenger is increased is calculated in cases G, H, I, J. The changes in the yields, expressed relative to the yield at the lowest concentration of scavenger, are shown in Fig. 5. The curve is qualitatively very similar to that for γ -ray spurs (I, Fig. 12) but the quantitative effect is somewhat smaller for cylindrical tracks than for the γ -ray spurs. This difference is also shown in the calculations of Ganguly and Magee (6). This arises because of the competition between the scavenging processes and the recombination processes. In the cylindrical tracks the recombination reaction occurs to a greater extent, and a given concentration of scavenger will have less effect here than in a spherical spur.

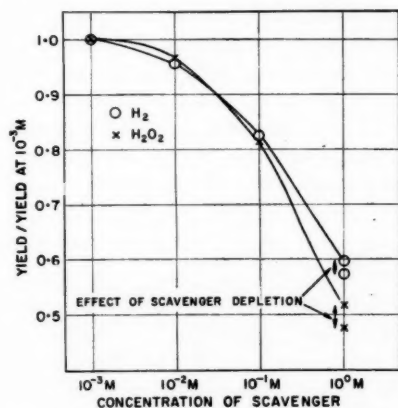


FIG. 5. Effects of scavenger concentration on the molecular yield. The abscissa is the ratio of $[H_2]$, $[H_2O_2]$ at the plotted scavenger concentration to the yield at $10^{-3} M$: $k_{18} = k_{28} = 1 \times 10^{-11}$ (cases G, H, I, J). The two lower points at $10^0 M$ represent the relative yields obtained if depletion of scavenger at the center of the track is neglected (case K).

Schwarz, Caffrey, and Scholes (4), Burton and Kurien (5), and Senvar and Hart (10) have made extensive studies of yields as a function of scavenger concentration and have found good agreement with the one-radical calculations of Ganguly and Magee and those of Fricke and Flanders (8). These simpler calculations are, at the present time, more suitable for experimental comparison than our two-radical calculations because of the smaller number of parameters in the calculation.

Figure 5 shows that the yields of $[H_2]$ and $[H_2O_2]$ are changed at varying rates by the addition of scavenger. The curve for $[H_2]$ is at first lower than that for $[H_2O_2]$, but rises above it again at higher scavenger concentrations. This effect is numerically small and barely significant. In comparing these results with experiment it should be noted that, in these calculations, the scavenger reacts with both species simultaneously. In many experimental cases the scavenger reacts primarily with one species (e.g. halide ion with OH) and the other radical is removed by a secondary product (e.g. hydrogen atom by halogen atom). The over-all scavenger effects will also be affected by the competition

between the primary recombination steps. For these reasons a detailed study of effects of scavenger concentration with variation in track density and differing values of k_{13} and k_{23} has been deferred until more experimental data is available.

The effect of depletion of scavenger can be seen from case K. Here k_{13} and k_{23} and C_3 have been chosen in such a way that the effective concentration of scavenger—measured by the products $k_{13}C_3$ and $k_{23}C_3$ —is the same as in case J even though C_3 is greater by a factor of 10^3 . The recombination is, in effect, taking place in a constant concentration of scavenger so that there is no significant depletion of the scavenger. As expected, the effect of scavenger is greater if depletion at the center of the track is neglected, i.e. the values of $[H_2]$ and $[H_2O_2]$ are less in K than they are in J. The effect is, however, small, changing the yields by only 5–10%. Qualitative arguments, comparing the initial concentration of radicals in the spur ($\sim 10 M$) with the concentration of scavenger, suggest that the effect would be quite large. The direct comparison of the initial concentration of radicals is therefore somewhat misleading. It should be noted that the major fraction of recombination takes place before much scavenging has taken place, i.e. the two reactions are not competing on an equal basis until some appreciable time has elapsed. During this time the track has expanded and reduced the concentration of radicals quite sharply. At longer times the effect of depletion at the center of the track is counteracted by the diffusion of radicals to regions of higher scavenger concentration.

The relatively small effects due to diffusion of scavenger are also demonstrated by comparing L and J. The diffusion constant for the scavenger D_3 is reduced by a factor 4 in L, and the yields are unchanged within the numerical accuracy of the calculation.

7. VARIATION IN YIELDS WITH TRACK DIAMETER

The geometrical factors in the diffusion process for spherical spurs and cylindrical tracks make a considerable difference in the sensitivity of yields to spur or track radius. In spherical spurs the yields are quite sharply reduced when R_1 and R_2 ($R = 1/\beta$ where β is the modulus of the Gaussian, see Section 3) are increased by a factor of 2. In cylindrical tracks, however, the yields are relatively insensitive to the initial track radius. The molecular yields change by only about 3% in cases P, Q, and R where R_1, R_2 change from 5 Å to 20 Å. For spherical spurs the yields are reduced by 60–80% over the same range (A, S, T, Table I, Part I). In spherical spurs where R_1 only is increased, R_2 being kept constant, $[H_2]$ decreases and $[H_2O_2]$ increases. A different effect is observed for cylindrical tracks. Here $[H_2]$, $[H_2O_2]$, and $[-H_2O]$ all increase as R_1 increases (Q, S, T). At the same time $[H]$ increases and $[OH]$ decreases. These effects arise because of the insensitivity of the yield to the initial spur radius and to the behavior of the recombination term $k_{12}(H)(OH)$, which affects the yields of $[H_2]$ and $[H_2O_2]$ strongly. By making R_1 greater than R_2 the value of this term is decreased and more like radicals are available for recombination. A comparison between γ -ray spurs and cylindrical tracks is made in Table II.

TABLE II
Ratio of yields for $R_1 = 10 \text{ Å}$ to $R_1 = 25 \text{ Å}$, ($R_2 = 10 \text{ Å}$)
(cases A, Z, Part I; cases Q, T, Part II)

	$[H_2]$	$[H_2O_2]$	$[-H_2O]$
γ -Ray spurs	2.0	0.65	0.70
Cylindrical tracks	0.84	0.67	0.75

These results are of considerable interest in connection with the interpretation of the different yields in light and heavy water. The most recent experimental work on the system is summarized by Dainton (7). For γ -rays it appears that $G(\text{H}_2) > G(\text{D}_2)$, $G(-\text{D}_2\text{O}) > G(-\text{H}_2\text{O})$, and $G(\text{radicals D}_2\text{O}) > G(\text{radicals H}_2\text{O})$. The discussion in Part I on these isotope effects was related to earlier experimental work which suggested that $G(-\text{D}_2\text{O}) < G(-\text{H}_2\text{O})$ and is consequently superseded by the experimental work reported by Dainton and his co-workers.

Dainton suggests that the change in yields can be explained by assuming that, initially, D atoms are more widely dispersed than H atoms, i.e. $R_1(\text{D}) > R_1(\text{H})$. The first line in Table I shows that a change in this direction does decrease $[\text{H}_2]$ and increase $[-\text{H}_2\text{O}]$ for γ -ray spurs. The effect is, however, partially inverted for cylindrical tracks, $[\text{H}_2]$ is increased as R_1 is increased. Measurement of D_2 yields for densely ionizing particles may therefore shed some light on the origin of isotope effects in water. It should also be noted that this change in R_1 affects the yield of $[\text{H}_2\text{O}_2]$ as well so that one would expect $G(\text{H}_2\text{O}_2) < G(\text{D}_2\text{O}_2)$. This inequality is found experimentally in some, but not all, of the aqueous systems which have been studied.

The mechanism proposed by Dainton to account for the larger displacement of D atoms requires some hydrogen atoms to be formed by the process: $e_{\text{aq}}^- + \text{H}_2\text{O} \rightarrow \text{H} + \text{OH}^-$. The Samuel-Magee model as originally proposed discounts this type of process.

8. GENERAL CRITIQUE OF THE SAMUEL-MAGEE MODEL

The original model proposed by Samuel and Magee can be modified in many ways without, in principle, changing the basic idea, namely that the radical and molecular yields arise from a bimolecular, diffusion-controlled reaction of H and OH. The inclusion of reactions between radicals and molecules and the concept of spatial correlation of the radicals (leading to time-dependent rate constants) are minor modifications to the kinetic scheme of the model. The principal criticism of the model is still that the mechanism of formation of free radicals H and OH from the initial ionized state ($\text{H}_2\text{O}^+ + e(100 \text{ ev})$) is neither established nor understood (12).

The model was originally advanced to explain the separation between radical and molecular yields of water. The relative values of these yields have been shown to be correctly predicted in a qualitative sense in the one-radical calculations cited elsewhere in this paper (1, 6, 8). The relative values of the yields of H_2O , H_2O_2 , H, OH are qualitatively predicted in the two-radical versions of the model described in this series of papers. The variation of molecular yields with scavenger concentration has been predicted semi-quantitatively in several treatments (6, 8, 9). The variation in yields with ionization density is, in its broad features, correctly predicted in the calculations of Ganguly and Magee and the two-radical model in this paper. These successes of the model are powerful arguments in favor of its validity. To be more specific, one can conclude from the comparison of theory and experiment that H_2 and H_2O_2 are formed by kinetically similar mechanisms and that these are bimolecular diffusion-controlled reactions, probably simple recombinations $\text{H} + \text{H}$, $\text{OH} + \text{OH}$, and $\text{H} + \text{OH}$.

On the other hand, the model, in the simple formulation discussed here, predicts neither the variations in yield with pH, nor the details of the yields at high-track density (inversion of the relations $[\text{H}_2] < [\text{H}_2\text{O}_2]$ and the increase in $G(-\text{H}_2\text{O})$) and does not explain the isotope effects. (We reject large *ad hoc* variations in rate constants as "explanations" of such effects.) Variations in yields with pH require the introduction of reactions involving hydrogen ions. These, however, are an elaboration of the kinetic

scheme and so do not alter its essence. Variations in yield at high-track density may also be explained by radical-molecule reactions, and/or by taking into account the spatial correlation of free radicals. These, again, elaborate the kinetic scheme, but do not, in principle, alter the model. The isotope effects cannot apparently be explained without some significant change in the kinetic scheme or of the constants and parameters in the system.

One of the more significant conclusions of these papers is that the use of gas-phase data to deduce the initial structure of spurs and tracks is, at best, misleading. Even after exercising the caution necessary when deducing a mechanism from kinetics, the qualitative successes of the model are very striking and lead us to believe that it describes correctly the majority of processes occurring in the life history of spurs and tracks. The model only does this, however, for spur sizes and radical densities that are significantly different from those deduced from gas-phase data. In Part I arguments are developed, from gas-phase data, showing that the "average" spur resulted from an energy deposition of 65 ± 10 ev and contained ~ 6 radical pairs/spur. The calculations in this part show, however, that an energy deposition of ~ 20 ev is required to produce one "effective" radical pair. This invalidates the use of Firestone's measurements on the radiolysis of water vapor to estimate the energy required to produce a radical pair in liquid water and, further, makes either the validity or the relevance of cloud-chamber data to determine the energy deposition/spur open to question. The discussions to be found in ref. 12 are still very pertinent to the present state of knowledge.

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APPENDIX

DIFFUSION WITH RECOMBINATION IN CYLINDRICAL GEOMETRY

(1) The Equations

The concentrations C_i of three types of particles are given by

$$[1] \quad \frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i - \sum_j k_{ij} C_i C_j$$

where the D_i are diffusion constants and the k_{ij} are rate constants for recombination reactions. The operator ∇^2 is the cylindrical Laplacian:

$$\nabla^2 \equiv \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r}.$$

Initially the particles of types 1 and 2 are confined to a small cylindrical region, while those of type 3 are uniformly distributed through all space:

$$C_i(r,0) = \frac{N_i \beta_i^2}{\pi} e^{-\beta_i^2 r^2}$$

for $i = 1, 2$.

$$[2] \quad C_3(r,0) = C_3,$$

where N_i is the number of particles per unit length and β_i the range parameter for type i .

We assume throughout that $k_{33} \equiv 0$.

The problem is the evaluation of the losses of particles (per unit length) due to the various modes of recombination:

$$\begin{aligned} [3] \quad L_{ij}(t) &= \int_0^t dt \int_0^\infty 2\pi k_{ij} C_i C_j r dr \\ &= \int_0^t \lambda_{ij}(t) dt. \end{aligned}$$

(2) Co-ordinate Transformations

Before attempting the numerical solution of the system [1] it is useful to make several changes of variable. We define new dependent variables by

$$[4] \quad X_i = t^{\frac{1}{2}} r^{\frac{1}{2}} C_i,$$

and introduce the expanding radial co-ordinate by

$$[5] \quad \rho = r/(D_1 t)^{\frac{1}{2}}$$

where (by convention) D_1 is the larger of D_1 and D_2 .

Equation [1] is transformed into

$$[6] \quad t \frac{\partial X_i}{\partial t} = \Delta_i \left[\frac{\partial^2 X_i}{\partial \rho^2} + \frac{1}{4\rho^2} X_i \right] + \frac{3}{4} X_i + \frac{\rho}{2} \frac{\partial X_i}{\partial \rho} - \frac{1}{\rho^{\frac{3}{2}} D_1^{\frac{1}{2}}} \sum_j k_{ij} X_i X_j.$$

These transformations are similar to the ones used previously in spherical geometry. Their utility arises from the fact that in the absence of recombination terms the solution that is initially

$$C_1(r, t_0) = A e^{-\beta_1^2 r^2}$$

at time t_0 makes the right side of (6) vanish provided t_0 is chosen so that

$$4\beta_1^2 D_1 t_0 = 1.$$

Thus the numerical work is devoted to examination of that part of the behavior that is not simple outward diffusion.

It is straightforward to verify that in the absence of recombination the equation for X_3 reduces to

$$t(\partial X_3/\partial t) = X_3$$

or

$$[7] \quad X_3 = \frac{t}{t_0} X_3(t_0).$$

The increase in X_3 is a consequence of the fact that in real space C_1 and C_2 at any point decrease like $1/t$ due to outward diffusion, so that the transformation that keeps these constant gives an apparent increase in X_3 corresponding to constant C_3 .

Finally, it is expeditious to introduce a new time variable x such that equal increments in x correspond to expanding steps in t . This is related to the physical fact that as time proceeds the concentrations and their gradients decrease, and we can afford to pursue them more vigorously. After some numerical experiments the choice made for spherical geometry was adopted.

$$[8] \quad t = t_0 e^x.$$

The final form of [6] is

$$[9] \quad \frac{\partial X_i}{\partial x} = \Delta_i \left[\frac{\partial^2 X_i}{\partial \rho^2} + \frac{1}{4\rho^2} X_i \right] + \frac{3}{4} + \frac{\rho}{2} \frac{\partial X_i}{\partial \rho} - \frac{1}{\rho^4 D_1} \sum_j k_{ij} X_i X_j.$$

(3) Solution of the Equations

The method of integration follows closely the method used for spherical geometry. Tables of X_1 , X_2 , X_3 at 40 values of ρ were used, and the space derivatives evaluated using the relations

$$[10] \quad \begin{aligned} \frac{\partial^2 X^{(n)}}{\partial \rho^2} + \frac{1}{4\rho^2} X^{(n)} &= \frac{1}{h^2} [X^{(n+1)} - T_n X^{(n)} + X^{(n-1)}] \\ \frac{\rho}{2} \frac{\partial X^{(n)}}{\partial \rho} &= \frac{n T_n}{8} [X^{(n+1)} - X^{(n-1)}] \end{aligned}$$

where h is the interval in the variable ρ , and

$$T_n = \left(1 - \frac{1}{n}\right)^{\frac{1}{2}} + \left(1 + \frac{1}{n}\right)^{\frac{1}{2}}.$$

The choice of T_n is related to a quirk of cylindrical geometry. The usual formula for the second derivative is

$$\frac{\partial^2 X^{(n)}}{\partial \rho^2} = \frac{1}{h^2} [X^{(n+1)} - 2X^{(n)} + X^{(n-1)}].$$

Now for large n ,

$$T_n = 2 - \frac{1}{4n^2} + \text{terms of order } \frac{1}{n^4};$$

hence the use of T_n in place of 2 compensates for the inclusion of $(1/4\rho^2)X$ in the Laplacian. Also, for small n , $X \sim \rho^{\frac{1}{2}}$, and its derivatives are not well represented by finite difference formulas due to the singularity at $\rho = 0$. The choice of T_n makes the formulas exact for the function $X = \rho^{\frac{1}{2}}$, and hence compensates for this difficulty.

When [12] is substituted into [11], we are left with a set of 120 first-order differential equations for $X_i^{(n)}(x)$ for $i = 1, 2, 3$, and $n = 0, 1, \dots, 39$. The integration is carried out by the second-order "midpoint" method already used for spherical geometry.

The initial conditions and boundary conditions are obtained from [2], applying the co-ordinate transformations [4] and [5].

$$X_i^{(n)}(0) = t^{\frac{1}{2}} r^{\frac{1}{2}} \frac{N_i \beta_i^2}{\pi} e^{-\beta_i^2 r^2}$$

for $i = 1, 2$. With $t = t_0$ and $\rho = nh$

$$[11] \quad X_i^{(n)}(0) = \frac{N_i \beta_i^2 t_0}{\pi} (nh)^{\frac{1}{2}} (D_1)^{\frac{1}{2}} e^{-\beta_i^2 D_1 t_0 n^2 h^2}.$$

It follows that $X_1^{(0)} = X_2^{(0)} = 0$ for all time, and we also impose the condition that $X_1^{(39)} = X_2^{(39)} = 0$ for all time. Naturally, h must be large enough that this cutoff at "infinity" leads to negligible error.

The initial condition for X_3 is

$$X_3^{(n)}(0) = t^{\frac{1}{2}} r^{\frac{1}{2}} C_3 \\ [12] \quad = t_0 (nh)^{\frac{1}{2}} D_1^{\frac{1}{2}} C_3.$$

Again $X_3^{(0)} = 0$ for all time. For the outer point $X_3^{(39)}$ we note that since X_1 and X_2 vanish here and $k_{33} \equiv 0$ there is no recombination. Thus equation [8] applies at the outer point, and

$$X_3^{(39)} = X_3^{(39)}(t_0) t/t_0 \\ [13] \quad = X_3^{(39)}(t_0) e^x.$$

(4) The Integrals

For the loss integrals, we use

$$L_{ij} = \sum_x \lambda_{ij}(x),$$

where the loss during any interval Δx is

$$\lambda_{ij} = \frac{dt}{dx} (\Delta x) \int_0^\infty 2\pi k_{ij} C_i C_j r dr \\ [14] \quad = 2\pi D^{\frac{1}{2}} (\Delta x) \int_0^\infty k_{ij} X_i X_j d\rho$$

after applying the transformation [4], [5], [8].

Similarly, the current values of the numbers of particles per unit length may be obtained from

$$N_i(x) = 2\pi \int_0^\infty C_i r dr \\ [15] \quad = 2\pi D_1^{\frac{1}{2}} \int_0^\infty X_i^{\frac{1}{2}} D_1^{\frac{1}{2}} d\rho.$$

The integrands in [14] and [15] are available as tables obtained during the solution of the equations. The integrals are evaluated by Simpson's rule.

(5) *Input and Output*

The input data are defined by a choice of

$$\begin{array}{ccccc} & t_0, & h = \Delta\rho, & \Delta x, & \\ k_{11}, & k_{22}, & k_{12}, & k_{13}, & k_{23}, \\ D_1, & D_2, & D_3, & & \\ N_1, & N_2, & \beta_1, & \beta_2, & C_3. \end{array}$$

It has been found that $\Delta x = 0.02$ is about the largest value that avoids instability in the solutions; $h = 0.3$ is a convenient choice. The value of t_0 depends on the physical parameters; it must set the pace of the co-ordinate system expansion to the pace of the actual diffusion. The "theoretically best" value is

$$t_0 = \frac{1}{4}\beta_1^2 D_1,$$

but it has been found that a rather smaller value

$$t \approx \frac{1}{6}\beta_1^2 D_1$$

avoids certain difficulties arising from the outer boundary conditions.

After every few steps in x (10 steps in most of the production runs), the following quantities are printed.

Elapsed time

$$\begin{array}{ccccc} L_{11} & L_{12} & L_{13} & N_1 & \Sigma_1 \\ L_{22} & L_{12} & L_{23} & N_2 & \Sigma_2, \end{array}$$

where Σ_i is the sum of the four other quantities in its row. Σ_i should be independent of t , and its constancy is a check on the stability of the solution.

(6) *Extrapolation to $t = \infty$*

The printed results emerge at equal increments in x . It turns out that if the results for L_{11} , L_{12} , L_{22} are plotted as a function of the variable

$$y = e^{-x/2} = \sqrt{t_0/(T+t_0)},$$

where T is the elapsed time, they lie very nearly on a straight line for small y (large T). Thus for any of these terms,

$$\begin{aligned} L_\infty &= L_F + \frac{y_F}{y_{F-1} - y_F} (L_F - L_{F-1}) \\ &= L_F + \frac{1}{(y_{F-1}/y_F) - 1} (L_F - L_{F-1}), \end{aligned}$$

where L_F and L_{F-1} are the last and the penultimate values.

Now $y_{F-1}/y_F = e^{\frac{1}{2}\Delta x}$, and we have used $\Delta x = 0.2$. Thus

$$[16] \quad L_\infty = L_F + 9.5 (L_F - L_{F-1}).$$

It should be remarked that there is no particular justification for this recipe other than the empirical straightness of a line. At best, L_∞ given by [16] may contain one more significant figure than would be obtained by taking $L_\infty = L_F$.

THE RADIOLYSIS OF SOME ORGANIC HALOGEN COMPOUNDS IN AQUEOUS SOLUTION¹

R. J. WOODS AND J. W. T. SPINKS

ABSTRACT

Dilute aqueous solutions of some halogen-substituted ethanols, acetaldehydes, and acetates have been irradiated with Co^{60} gamma rays, and the yield of acid products determined. Irradiations were carried out using air-saturated solutions and also solutions from which the air had been displaced by nitrogen or hydrogen. The acid yields are correlated with the structure of the organic compounds.

INTRODUCTION

The action of ionizing radiations on certain organic chloro-compounds has been studied extensively, both in aqueous solution and as two-phase systems with water, with a view to their use as chemical dosimeters, though little consideration has been given to the chemical reactions taking place (1). Two-phase systems of chloroform or tetrachloroethylene with water have received most attention; when irradiated in the presence of air both give high yields of hydrochloric acid which are directly proportional to the dose of radiation received. The acid is formed by a chain reaction and the yields are dependent on the temperature, dose rate, and energy of the incident radiation, and are lowered by traces of impurities. These variables curtail the usefulness of the systems for dosimetry; their effect may be reduced by increasing the proportion of water in the system, for example by using dilute aqueous solutions of the organic compounds, though the amount of acid formed by a given dose of radiation falls if this is done. However, the ease with which acid can be determined in an aqueous solution suggested that it would be worth while to measure the acid formed from solutions of other organic halogen compounds on irradiation, and attempt to correlate the yield of acid with the structure of the compound. The halogen-substituted hydrocarbons are normally only slightly soluble in water but by substituting a suitable group, which for convenience will be referred to as the functional group, in the molecule, water-soluble compounds can be obtained. The present study employs a series of halogen-substituted ethanols, acetaldehydes, and acetates in which the functional groups are hydroxymethyl, aldehyde, and carboxylate respectively.

The compounds were irradiated as 0.1 molar solutions of the neutral compounds and 0.1 normal solutions of the barium salts of the substituted acids. Yields of acid were determined by titration with aqueous alkali and yields of halide ion, other than fluoride, by titration with silver nitrate solution; fluoride was estimated by a colorimetric method. Results are given to show the effect upon the acid yield of varying the dose rate and of displacing the air normally present by nitrogen or hydrogen, since previous work had shown that the yield from trichloroacetaldehyde (chloral) (2) and tribromoacetaldehyde (bromal) (3) was dependent upon the dose rate and the presence of oxygen. Some estimates of the oxygen consumed during radiolysis are given.

Experiment showed that the halogen was liberated as halide from every compound examined, though the yields of fluoride from fluorine-substituted compounds were generally

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low. The acid yields are discussed with reference to the structure of the compounds irradiated. The use of these halogen-substituted compounds in chemical dosimetry is discussed briefly.

EXPERIMENTAL

Materials

The distilled water used was redistilled from alkaline permanganate and then from acid dichromate solutions and stored in Pyrex bottles.

Reagent grade chemicals were used when these were available commercially. Materials of lower grade, and products prepared in the laboratory, were purified by crystallization to constant melting point or by repeated distillation, until the main fraction had a boiling range of less than 2° C. The purity of several of the bromo-compounds could be checked by treating them (10–20 mg) with excess 0.1 *N* sodium hydroxide solution and titrating the excess of alkali after a suitable interval (see Table VI) (cf. ref. 3). Equivalent weights determined in this way are given after the preparation of the appropriate compound. Whenever possible the radiolysis yields from two separate batches of a given compound were compared; in no case were there serious differences in yield between the different samples.

Reagent grade chloroform was washed 10 times by shaking with distilled water, distilled, and stored under water, in the dark.

Trifluoroacetaldehyde

Trifluoroacetaldehyde hydrate (fluoral hydrate), prepared from trifluoroacetic acid (4), was fractionated and the fraction, b.p. 103–105° C, dehydrated with hot, concentrated sulphuric acid. The gaseous fluoral was absorbed in a little less than the theoretical amount of water and the crystalline hydrate, which separated, filtered off, and dried over phosphorus pentoxide, m.p. 66–66.5° C.

Bromoacetaldehydes

The bromoacetaldehydes were prepared by brominating paraldehyde (5); omitting the sulphur catalyst, since this increased the quantity of tarry residue formed without markedly improving the yield of products, and distilling the volatile products from the reaction vessel under reduced pressure and as rapidly as possible when the reaction was complete. The distillate was carefully fractionated under reduced pressure to give monobromoacetaldehyde, b.p. 52–53° C/57–62 mm, dibromoacetaldehyde, b.p. 61–64° C/58–62 mm, and tribromoacetaldehyde (bromal), b.p. 43–45° C/4–5 mm.

The proportions of the three bromoacetaldehydes formed varied with the proportions of the reactants used and with the conditions of the bromination. For example, when 1360 g bromine (8.5 moles) was added dropwise to 193 g paraldehyde (equivalent to 4.4 moles of acetaldehyde) diluted with 400 ml carbon tetrachloride over a period of 4 hours and the mixture warmed to 50° C for a further 1 hour the products were 124 g monobromoacetaldehyde (1.0 mole), 300 g dibromoacetaldehyde (1.5 moles), and 179 g bromal (0.65 mole). The theoretical quantity of bromine, added to the paraldehyde-carbon tetrachloride mixture while it was being cooled with a cold-water bath, gave monobromoacetaldehyde in 80% yield. The proportion of bromal in the products could be increased by using a molar ratio of bromine to paraldehyde of 3:1 and stirring the reaction mixture at 50° C for several hours after adding the bromine: the products always included some dibromoacetaldehyde.

Both monobromoacetaldehyde and dibromoacetaldehyde polymerized on standing

and, for convenience, were converted into the stable hydrates immediately after distillation by being stirred with a small excess of water. Seed crystals to initiate crystallization of monobromoacetaldehyde hydrate were obtained by distilling a portion of the aldehyde-water mixture; the distillate (b.p. $97^{\circ}/720$ mm) crystallized in the condenser. Monobromoacetaldehyde hydrate crystallized from water as needles; m.p. between 61 and 95° C, depending upon the rate of heating. Dibromoacetaldehyde hydrate crystallized from water as needles, m.p. 61 – 61.5° C. (Found: equiv. wt., 75.1 . Calc. for $C_2H_4O_2Br_2$: equiv. wt., 73.3 .) Bromal hydrate, m.p. 54° C. (Found: equiv. wt., 294 . Calc. for $C_2H_3O_2Br_3$: equiv. wt., 299 .)

Tribromoacetic Acid

Fuming nitric acid (30 ml) was added dropwise, through a reflux condenser, to bromal (100 g) which was warmed to about 70° C with a warm-water bath. When the addition was complete (15 minutes) the temperature of the water bath was raised to 90 – 100° C and the reaction mixture kept at this temperature for 3 hours. Removal of the volatile materials by distillation under reduced pressure (90° C/ 30 mm) left a residue of white crystals which were recrystallized from a mixture of benzene and light petroleum to give tribromoacetic acid as white plates (88 g), m.p. 127.5° C, unchanged by further recrystallization. Found: equiv. wt., 291 . Calc. for $C_2HO_2Br_3$: equiv. wt., 297 . A further quantity of pure acid was recovered from the mother liquors (5 g; total yield 88% theoretical).

Dibromoacetic Acid

(a) Fuming nitric acid (15 ml) was added cautiously to dibromoacetaldehyde hydrate (26 g) contained in a flask fitted with a reflux condenser and heated in a boiling-water bath. The heating was continued for 1 hour after the acid had been added. The products were fractionated under reduced pressure, and the fraction collected, b.p. 123 – 125° C/ 17 mm (20.4 g; 77% theoretical). Found: equiv. wt., 221 . Calc. for $C_2H_2O_2Br_2$: equiv. wt., 218 . The acid solidified on standing (m.p. about 36° C) and could be crystallized, with difficulty, from light petroleum. The crystals were very deliquescent and the acid was more conveniently purified by distillation.

(b) (Cf. ref. 6, which gives the preparation of dichloroacetic acid from chloral hydrate.) To a solution of bromal hydrate (45 g) in water (45 ml), warmed to 50° C, were added calcium carbonate (15.3 g) and a solution of sodium cyanide (1 g) in water (3 ml). The mixture was shaken and allowed to stand at room temperature until its temperature, which slowly rose to 74° C after the cyanide had been added, started to fall. Isopropanol (1–2 ml) was added to curb frothing and the mixture gently refluxed for 20–30 minutes, cooled, and extracted with ether. The ether extract was dried over magnesium sulphate, the ether evaporated, and the residue fractionated under reduced pressure to give dibromoacetic acid, b.p. 109 – 111° C/ 10 mm (24.9 g; 76% theoretical) as a colorless liquid which rapidly solidified. Found: equiv. wt., 222 .

Substituted Ethanols

2,2,2-Trichloroethanol was prepared by reducing chloral with either aluminum isopropoxide (7) or lithium aluminum hydride (8); both reactants gave the pure alcohol, b.p. 148° C/ 705 mm, 73° C/ 35 mm, in about 65% yield.

Reduction of bromal in a similar manner with either aluminum isopropoxide or lithium aluminum hydride gave 2,2,2-tribromoethanol as colorless crystals, m.p., after recrystallization from water or a mixture of benzene and light petroleum, 78° C. Found: equiv. wt., 93.5 . Calc. for $C_2H_3OBr_3$: equiv. wt., 94.3 . The yields of pure alcohol were about 60% and 20% respectively.

Reduction of dibromoacetaldehyde with aluminum isopropoxide gave 2,2-dibromoethanol, b.p. 66–67° C/3 mm (57% theoretical). Found: equiv. wt., 101. Calc. for $C_2H_4OBr_2$: equiv. wt., 102.

Chlorodifluoroacetic Acid and Dichlorofluoroacetic Acid

These acids were obtained from L. Light and Co. Ltd., Poyle Trading Estate, Colnbrook, Bucks, England, and were redistilled before use. The chlorodifluoroacetic acid had b.p. 124–126° C and the dichlorofluoroacetic acid b.p. 156–158° C.

Barium Salts

The acids were generally irradiated as solutions of the barium salt so that the pH of the solutions would be comparable to those of the neutral halogen compounds. The salt solutions were prepared either from the pure crystalline salt or by making up a standard solution of the acid in the presence of an excess of pure barium carbonate, subsequently filtering off the excess carbonate, and drawing a current of moisture-saturated air through the solution to bring it into equilibrium with the atmosphere. The crystalline salts were prepared by adding an excess of pure barium carbonate to aqueous solutions of the pure (chloroacetic) acids, filtering off the excess carbonate, and allowing the neutral solutions partially to evaporate at room temperature; higher temperatures caused some decomposition. The crystals deposited were collected, washed with water, and dried over phosphorus pentoxide; the barium content was determined gravimetrically by precipitation with dilute sulphuric acid. Found: Ba, 30.3, 30.3. Calc. for $C_4O_4Cl_6Ba$: Ba, 29.7%. Found: Ba, 35.8, 35.6. Calc. for $C_4H_2O_4Cl_4Ba$: Ba, 34.95%. Found: Ba, 41.0, 41.0. Calc. for $C_4H_4O_4Cl_2Ba$: Ba, 42.35%. The yield of acid obtained on irradiation was the same by whichever method the salt solution was prepared.

The calcium salts of dibromo- and tribromo-acetic acids and of trichloroacetic acid, prepared by adding calcium carbonate to a standard solution of the acid, were also irradiated, with results in good agreement with those obtained using solutions of the barium salts.

Irradiations

Irradiations were carried out using Co^{60} sources of about 1 and 90 curies, respectively. Dose rates were measured using the ferrous sulphate dosimeter (9), assuming a G value of 15.5 for the formation of ferric ion.

As far as possible solutions were prepared immediately before use; the pH of the solutions was measured using a Beckman model M pH meter. Aliquots (3.0 ml) were irradiated at room temperature in stoppered glass test tubes, 13×100 mm, supported in lucite blocks arranged concentrically about the 90-curie source or else supported in a water bath surrounding the 1-curie source.

The acid formed on irradiation was determined as described earlier (3), by titration with either 0.1 N sodium hydroxide solution (bromophenol blue) or 0.01 N silver nitrate solution (eosin). Occasionally the bromophenol blue was partially bleached when added to solutions which had been irradiated for a long time, the color change making it difficult to decide when the irradiated solution being titrated matched the color of the blank. The difficulty could be partly overcome by allowing the irradiated solution to stand for 1 or 2 hours before being titrated, and may be caused by peroxides formed on irradiation; neither bromine nor chlorine have been detected in the irradiated solutions. It was noted previously (3) that solutions of bromal might be titrated up to 24 hours after irradiation without change in the titer. When potassium iodide was added to solutions of bromal which had been irradiated, a little iodine was liberated immediately and larger amounts

were liberated on standing; the iodine was estimated by titration with 0.1 *N* sodium thiosulphate solution using a starch indicator. Iodine formed in solutions of iodoacetate by irradiation was estimated in the same way.

If the compound being irradiated was relatively stable to alkali, for example the substituted acetates, the acid formed could be titrated using an indicator changing color at a higher pH than bromophenol blue; bromocresol purple, bromothymol blue, and phenolphthalein were used to determine acid products that would not be neutralized at the bromophenol blue end point. However, difficulty was sometimes experienced in reaching a stable end point with these indicators, when it appeared that alkali-labile products were being slowly hydrolyzed by the alkali added; stable end points could be reached eventually by adding alkali as required, over a period of several minutes.

Fluoride was estimated by its action in bleaching a zirconium-alizarin red lake, measured with a photoelectric colorimeter (Megregian-Maier method) (10).

Solutions irradiated in the absence of air were treated before irradiation by passing a stream of either nitrogen or hydrogen through aliquots of the solution contained in irradiation tubes sealed with rubber serum-bottle caps. The gases were introduced into the tubes through a glass capillary which was pushed through the rubber cap, and escaped through a hypodermic needle inserted in the cap; a piece of adhesive tape effectively sealed the small holes left when the capillary and needle were removed. Traces of oxygen were removed from the nitrogen by passage through an alkaline solution of sodium hydro-sulphite containing a catalytic amount of anthraquinone 2-sulphonate and from the hydrogen by passing it through a catalytic deoxidizer. Both gases were washed with water before being passed into the aliquots, which were purged for from 10 to 20 minutes; the shortest period of purging to ensure consistent results was about 5 minutes. An air-saturated solution of bromal gave the same yield of acid when irradiated in tubes sealed with glass stoppers or rubber serum-bottle caps.

Fluoral hydrate solutions were irradiated in both glass test tubes and in lusteroid tubes; the same acid yield was found in both cases.

The acid produced, in terms of microequivalents per liter, was plotted against the dose in kilorads and the slope of the straight line measured to give the acid yield in microequivalents per liter per kilorad. Each point on the graph was the average value of the acid produced for two or three duplicate irradiations; from 6 to 10 points were used to determine the slope of the line. Acid yields were found to be reproducible to $\pm 10\%$, or better, with different batches of material and for duplicate determinations at intervals of several months.

RESULTS

Acid yields in terms of microequivalents per liter per kilorad were multiplied by 0.945 to convert them to *G* values; the factor was derived in a similar manner to the factor used previously (3) to convert acid yields from microequivalents per liter per kiloroentgen to *G* values; it also includes a small correction for the difference in energy absorption of the ferrous sulphate dosimeter solution and the solutions of the halogen compounds. The errors introduced by using a single, average, value of the conversion factor for the solutions of slightly different density and electron density were estimated to be not more than 1% and may be discounted in view of the larger experimental uncertainty already present.

Acid Yield from Air-saturated Solutions

Table I gives the yield of acid from the compounds studied, determined by titration with sodium hydroxide solution, and, in parentheses, the yield of halide ion.

The indicator used in the acid-base titrations, bromophenol blue, was such that strongly acid products, for example the halogen-substituted acetic acids, would be neutralized while weak acids, acetic acid and carbon dioxide, would not. When both acid yield and halide yield (other than fluoride) were determined for the same compound it was found that the acid yield was the larger for the substituted aldehydes and alcohols and the smaller for the substituted acids. The acid yield was greater than the halide yield by about 18% for air-saturated solutions of bromal hydrate (cf. ref. 11) and tribromoethanol and by about 25% for solutions of dibromoacetaldehyde, showing that besides hydrobromic acid appreciable quantities of other strongly acid products are formed from these compounds; these products are probably bromine-substituted acetic acids. It has been reported that the yield of acid from aqueous solutions of chloral hydrate is about 30% greater than the yield of chloride when they are irradiated with either Co^{60} gamma rays (12, 13) or Sr^{90} beta rays (13). No systematic attempt has been made to determine weakly acid products from our irradiations; a single determination of the acid formed from a solution of bromal hydrate (1020 rads/min) using both bromophenol blue and bromocresol purple as indicators gave a 17% greater yield with the latter indicator; carbon dioxide was removed from the solution before titrating. The yield of acid from the bromoacetates was from 30 to 50% lower than the yield of bromide, part of the organic acid originally present being converted to neutral products during the irradiation; carbon dioxide in the products was estimated approximately and was found sufficient to account for the loss of the acid groups by decarboxylation. Irradiated solutions of dibromoacetate and tribromoacetate, freed of carbon dioxide and titrated with alkali, gave the same titer when either bromophenol blue or phenolphthalein was used as indicator; thus weakly acid products were not formed and the bromoacetic acid originally present was not, in effect, neutralized by being converted to a much weaker acid. The negative G value shown for trifluoroacetate means that more acid was lost by decarboxylation than was formed by breakage of the carbon-fluorine bond.

Poor results were obtained when monobromoacetate was irradiated at low dose rates because of partial hydrolysis of the acid during the long periods of irradiation; at higher dose rates the irradiation times were shorter and the hydrolysis less important. Iodine liberated from monoiodoacetate appeared partly as iodide ion and partly as molecular iodine; the G values for each are given in Table I.

Hayon and Weiss (14) have irradiated monochloroacetic acid solutions with X-rays and report G_{Cl^-} values from 2 to 8 for air-saturated solutions (0.01 to 1 M) and 0.9 for deaerated solutions (0.1 M). They also report G_{Cl^-} 6 to 16 for deaerated solutions of trichloroacetic acid over the concentration range 10^{-2} to 1 molar (cf. Table III).

The concentration of the chloroform solution was limited to that of a saturated solution at the temperature of the experiment, i.e. 0.07 molar. However, both 0.07 molar and 0.1 molar solutions gave the same acid yield in the following instances: trichloroethanol, irradiated at 1020 and 17 rads/min, and chloral hydrate and trichloroacetate, irradiated at 1020 rads/min, and the G values for chloroform are directly comparable with the other values in Table I. Taplin (1) gives G_{acid} 25.5 and Teplý and Bednář (15) G_{Cl^-} 25.8 ± 1.3 for air-saturated chloroform solutions irradiated under conditions comparable to those for the values in Table I; the latter authors determined the acid produced in several ways and it appears that for chloroform the yield of acid and the yield of chloride are the same. Teplý and Bednář also give G_{CO_2} 8.4 for air-saturated chloroform solutions and G_{Cl^-} 6.3 for solutions from which the air had been displaced by nitrogen.

Acid Yield in the Absence of Oxygen

When the amount of acid produced was plotted against the dose of radiation received

TABLE I

Yield of acid from aqueous solutions of organic halogen compounds on irradiation*

Compound	G_{acid} dose rate		
	1020 rads/min	450 rads/min	17 rads/min
Aldehydes			
$\text{Br}_3\text{C} \cdot \text{CH}(\text{OH})_2$	80 (69)	114 (98)	440 (360)
$\text{Br}_2\text{CH} \cdot \text{CH}(\text{OH})_2$	24.5 (21)	25.5 (21.5)	51.5 (35)
$\text{BrCH}_2 \cdot \text{CH}(\text{OH})_2$			(34)
$\text{Cl}_3\text{C} \cdot \text{CH}(\text{OH})_2$	43	50	112
$\text{F}_3\text{C} \cdot \text{CH}(\text{OH})_2$	6.7 (~1.5)		7.1
Alcohols			
$\text{Br}_3\text{C} \cdot \text{CH}_2\text{OH}$	36.5 (31)	38 (32)	104 (89)
$\text{Br}_2\text{CH} \cdot \text{CH}_2\text{OH}$			(31.5)
$\text{BrCH}_2 \cdot \text{CH}_2\text{OH}$			(9.5)
$\text{Cl}_3\text{C} \cdot \text{CH}_2\text{OH}$	24.5		27
Hydrocarbon			
Cl_3CH	27†		27†
Acids			
$\text{ICH}_2 \cdot \text{COOH}$	(2.6)		(9.2)
	(G_{12} , 1.4)		(G_{12} , 0.6)
$\text{Br}_3\text{C} \cdot \text{COOH}$	23 (41)	17.5 (38)	21 (39)
$\text{Br}_2\text{CH} \cdot \text{COOH}$	9.2 (17.5)		15.5 (20.5)
$\text{BrCH}_2 \cdot \text{COOH}$	4.2 (6.6)		18? (27?)
$\text{Cl}_3\text{C} \cdot \text{COOH}$	16		15.5
$\text{Cl}_2\text{CH} \cdot \text{COOH}$	12		12
$\text{ClCH}_2 \cdot \text{COOH}$	4.2		8.9
$\text{Cl}_2\text{CF} \cdot \text{COOH}$	7.2 (F^- , 0.8)	7.3	7.3
$\text{ClCF}_2 \cdot \text{COOH}$	5.1 (F^- , 2.9)	4.9	6.8
$\text{F}_3\text{C} \cdot \text{COOH}$	-1.9 (0.04)		

Values of $G_{\text{halide ion}}$ are given in parentheses.*Air-saturated 0.1 molar solutions, pH 3.5-5, $21 \pm 2^\circ \text{C}$. The acids were irradiated as 0.1 normal solutions of the barium salt.

†A saturated aqueous solution of chloroform was used; 0.07 M.

a straight line was obtained whose slope was a measure of the yield of acid. If the irradiation was continued long enough a rather abrupt change in the slope of the line occurred, the slope after the break corresponding to a lower yield, or G value, than that found initially. The break has been correlated with the point at which oxygen originally present in the solution has been used up (2, 3), the rather abrupt nature of the change in slope showing that the concentration of oxygen is not important. After the break was reached the yield of acid was that from a solution deficient in oxygen; the break did not appear with irradiations in which the acid was formed very slowly, for example solutions of monochloroacetate irradiated at low dose rates, when sufficient oxygen could diffuse into the solution to meet the needs of the reaction. Apart from such cases the break was found with solutions of all of the halogen compounds studied.

Table II gives the acid yield from solutions of bromal hydrate both before and after the break corresponding to exhaustion of the oxygen present; the latter yields were variable, from experiment to experiment, since the rate at which oxygen diffused into the solutions was not controlled. For comparison acid yields are included for solutions from which the air had been displaced by nitrogen; these yields were lower than those for the oxygen-depleted solutions, though the difference became smaller as the dose rate was increased, increasing the rate of the radiolysis reactions but not the rate of oxygen diffusion. In Table III are given acid yields from solutions saturated with either air or nitrogen.

Acid yields obtained from nitrogen-saturated and hydrogen-saturated solutions are

compared in Table IV. In the presence of hydrogen the ratio of hydroxyl radicals to hydrogen atoms, formed initially in definite proportions by the action of the radiation upon the water, may be altered in favor of the hydrogen atoms by the reaction (16),



TABLE II

The effect of oxygen depletion on the yield of acid from bromal hydrate solutions*

Dose rate (rads/min)	G_{acid}		
	Air-saturated solutions	Oxygen depleted	Air displaced by nitrogen
17	440 (360)	63-87 (87-130)	27.5 (20.5)
166	138	32	19.5
450	114	34	16
1020	82.5 (69.5)	17.5-20.5 (14)	16 (12)

Values of $G_{\text{halide ion}}$ are given in parentheses.

*0.1 molar solutions, pH 3.5-5, $21 \pm 2^\circ \text{C}$.

TABLE III

Yield of acid from organic halogen compounds irradiated in solutions saturated with either air or nitrogen*

Compound	G_{acid}		
	Nitrogen-saturated solutions		
	Air-saturated solutions (17 rads/min)	(17 rads/min)	(1020 rads/min)
$\text{Br}_3\text{C} \cdot \text{CH}(\text{OH})_2$	440 (360)	27.5 (20.5)	16 (12)
$\text{Br}_2\text{CH} \cdot \text{CH}(\text{OH})_2$	51.5 (35)	(16)	
$\text{Cl}_3\text{C} \cdot \text{CH}(\text{OH})_2$	112	19.5	
$\text{Br}_3\text{C} \cdot \text{CH}_2\text{OH}$	104 (89)	(18)	
$\text{Cl}_3\text{C} \cdot \text{CH}_2\text{OH}$	27	13.5	
$\text{Br}_3\text{C} \cdot \text{COOH}$	21 (39)	(14)	(10)
$\text{Br}_2\text{CH} \cdot \text{COOH}$	15.5 (20.5)	9.1 (16.5)	6.0
$\text{Cl}_3\text{C} \cdot \text{COOH}$	15.5	7.2	7.4
$\text{Cl}_2\text{CH} \cdot \text{COOH}$	12	5.4	4.5
$\text{ClCH}_2 \cdot \text{COOH}$	8.9	5.6	3.2
$\text{Cl}_2\text{CF} \cdot \text{COOH}$	7.3	8.2	6.9 (F^- , 0.25)
$\text{ClCF}_2 \cdot \text{COOH}$	6.8	3.7	4.0 (F^- , 0.7)
$\text{F}_3\text{C} \cdot \text{COOH}$			-4.9

Values of $G_{\text{halide ion}}$ are given in parentheses.

*0.1 molar solutions, pH 3.5-5, $21 \pm 2^\circ \text{C}$. The acids were irradiated as 0.1 normal solutions of the barium salt.

TABLE IV

Yield of acid from organic halogen compounds irradiated in solutions saturated with either nitrogen or hydrogen*

Compound	G_{acid}	
	Nitrogen-saturated solutions	Hydrogen-saturated solutions
$\text{Br}_3\text{C} \cdot \text{CH}(\text{OH})_2$	(20.7)	(19.8)
$\text{Br}_2\text{CH} \cdot \text{CH}(\text{OH})_2$	(15.8)	(15.0)
$\text{Br}_3\text{C} \cdot \text{CH}_2\text{OH}$	(18.2)	(19.1)
$\text{Br}_3\text{C} \cdot \text{COOH}$	(13.9)	(13.6)
$\text{Br}_2\text{CH} \cdot \text{COOH}$	6.0† (10.0†)	6.0† (9.9†)
$\text{Cl}_3\text{C} \cdot \text{COOH}$	7.2	6.9
$\text{Cl}_2\text{CH} \cdot \text{COOH}$	5.4	5.1
$\text{ClCH}_2 \cdot \text{COOH}$	5.6	5.5

Values of $G_{\text{halide ion}}$ are given in parentheses.

*0.1 molar solutions, pH 3.5-5, $21 \pm 2^\circ \text{C}$. The acids were irradiated as 0.1 normal solutions of the barium salt. Dose rate, 17 rads/min.

†Solutions irradiated at a dose rate of 1020 rads/min.

Hydrogen atoms and hydroxyl radicals would be expected to react differently with the halogen compounds and the absence of any marked difference between the yields for nitrogen- and hydrogen-saturated solutions suggests that at the low hydrogen concentrations used (about 10^{-3} M) the hydroxyl radicals react with the organic molecules in preference to hydrogen.

The ratio of the acid produced to the oxygen consumed could be estimated approximately from the position of the break in the graph, assuming that the solutions irradiated contained dissolved oxygen equal in amount to that in water under the same conditions of temperature and pressure; Table V gives some values estimated in this way. The values are the average for four or five experiments except for bromal hydrate when 30 values, distributed between the three dose-rate ranges shown, were available; the values were generally reproducible to within ± 0.5 unit, though they were not precise enough to show a consistent difference in a ratio when it was determined from the yield of acid and the yield of bromide separately. For bromal hydrate the ratio increased as the dose rate was increased; increasing the dose rate lowers the chain length of the chain-reaction forming acid and it may be inferred that less oxygen was consumed, relative to the amount of acid produced, in the chain-terminating steps than in the propagating steps. The values given in Table V show a tendency for less acid to be formed, relative to the oxygen used up, as the functional group was changed from $-\text{CH}(\text{OH})_2$ (or H) to $-\text{CH}_2\text{OH}$ and $-\text{COOH}$. The ratio was also lowered when a bromine atom of bromal hydrate was replaced by hydrogen to give dibromoacetaldehyde. Teplý and Bednář (15) give a ratio for chloroform of 3.9–4.7 equivalents of hydrochloric acid formed per molecule of oxygen used up, estimated in the same way.

TABLE V
Ratio of the acid produced to the oxygen used up*

Compound	Acid groups estimated	Dose rate (rads/min)	Equivalents of acid gained Molecules of oxygen used up
$\text{Br}_3\text{C} \cdot \text{CH}(\text{OH})_2$	HBr and total acid	9–18	3.0 ± 0.5
		160–450	3.6
		880–1460	4.0
$\text{Cl}_3\text{C} \cdot \text{CH}(\text{OH})_2$	Total acid	1020	4.1
Cl_3CH	Total acid	1020	4.2
$\text{Br}_3\text{C} \cdot \text{CH}_2\text{OH}$	HBr and	9–1020	3.6
	total acid		
$\text{Cl}_3\text{C} \cdot \text{CH}_2\text{OH}$	Total acid	1020	3.1
$\text{Br}_3\text{C} \cdot \text{COOH}$	HBr	1020	2.8
$\text{Cl}_3\text{C} \cdot \text{COOH}$	Acid change	1020	2.3
$\text{Br}_2\text{CH} \cdot \text{CH}(\text{OH})_2$	HBr and	390–1020	2.2
	total acid		

*Air-saturated 0.1 molar solutions, pH 3.5–5, $21 \pm 2^\circ \text{C}$. The acids were irradiated as 0.1 normal solutions of the barium salt.

Peroxides have been detected in irradiated solutions of the substituted acetates and of bromal hydrate; potassium iodide added to the latter solutions gave some iodine immediately and a greater amount on standing for several hours, the iodine formed immediately corresponded to hydrogen peroxide present in solution and that formed on standing to organic peroxides present. The concentration of hydrogen peroxide in the bromal solutions (dose rate 1020 rads/min) reached a low equilibrium value and then remained constant, but the concentration of organic peroxide increased in proportion to the dose of radiation received with a G value of about 12.

Effect of Dose Rate

The effect of changing the dose rate upon the yield of acid products has been examined by determining yields at two or three standard dose rates (cf. Tables I, II, and III). In the absence of oxygen, changes in dose rate had only a slight effect; a larger effect was observed in the presence of oxygen but only for those compounds which gave a high yield of acid products, indicative of a chain reaction, and then only at those dose rates at which the chain reaction was postulated. Dibromoacetaldehyde (Fig. 1) and tribromoethanol, for example, showed a dose rate dependency at dose rates in the region of 17 rads/min, but the acid yields were almost independent of dose rate between 450 and 1020 rads/min.

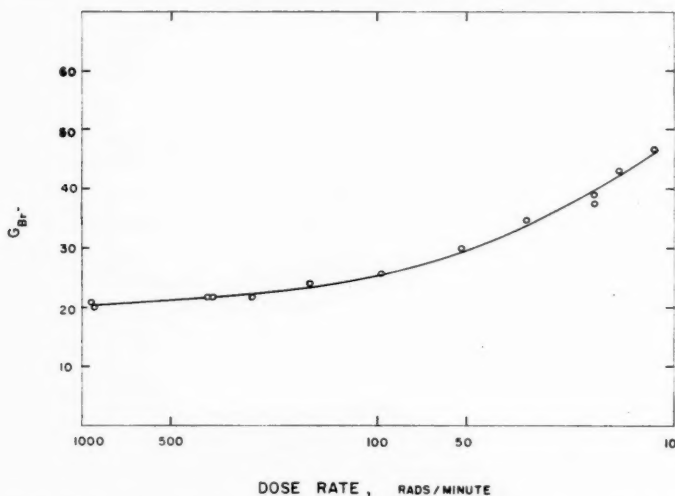


FIG. 1. Variation in G_{Br^-} with dose rate. Irradiation of 0.1 molar dibromoacetaldehyde hydrate solution, pH 4.2, 19°C.

Other work has shown that for dose rates in the range 1 to 60 rads/min G_{acid} for chloral hydrate (2) and bromal hydrate (3) was inversely proportional to the square root of the dose rate. The present work shows that this relationship is not obeyed closely at higher dose rates and it is possible that the yield of acid becomes independent of the dose rate as this is increased still further. The square root relationship was explained by postulating a chain reaction in which the termination step was the combination of two of the chain-propagating free radical intermediates to give a stable product; as the dose rate is increased the concentration of free radicals becomes greater and the chain length shorter. When the concentration of radicals becomes sufficiently high the chain length will approach unity and, unless the radicals interfere with the propagating steps, the acid yield will approach a constant value as the dose rate is increased. It is noteworthy that G_{acid} values for dibromoacetaldehyde and tribromoethanol, when they have reached the stage of being almost independent of dose rate, and some other dose rate independent G_{acid} values in Table I are greater than the sum of the probable G_H and G_{OH} values for water (about 5-6) and hence, if these inorganic radicals are responsible for the chemical changes occurring upon irradiation, each inorganic radical must be able to initiate reactions leading to the formation of several molecules of acid.

Action of Alkali on the Halogen Compounds

Most of the halogen compounds listed in Table I react readily with dilute aqueous alkali and these reactions were used as the basis for estimating the purity of several of the bromo-compounds (cf. ref. 3); a summary of the results is given in Table VI.

TABLE VI
Reaction of bromo-compounds with aqueous alkali*

Compound	Equiv. NaOH neutralized Mole of compound	Estimated time for complete reaction
Br ₃ C. CH(OH) ₂	1.0	Less than 1 minute
Br ₂ CH. CH(OH) ₂	3.0	3-5 minutes
BrCH ₂ . CH(OH) ₂	About 1.5	1-2 hours
Br ₃ C. CH ₂ OH	3.0	5 hours
Br ₂ CH. CH ₂ OH	2	5 hours
BrCH ₂ . CH ₂ OH	1	5-10 minutes
Br ₃ C. COOH	1.0	Neutralized immediately, about 3% hydrolysis and fission in 4 hours
Br ₂ CH. COOH	1.0	Neutralized immediately, about 1% hydrolysis in 18 hours
BrCH ₂ . COOH	2.0	Less than 1 minute

*Excess 0.1 N sodium hydroxide solution, titrated after reaction using phenolphthalein as indicator.

DISCUSSION

Effect of Structure on Acid Yield

Table I shows that for air-saturated solutions of the compounds studied the acid yield falls as (i) a halogen atom is replaced by hydrogen or by a more electronegative halogen, and (ii) as the functional group is changed from —CH(OH)₂ to —CH₂OH, to —COO⁻. The acid yield from the one substituted hydrocarbon included, chloroform, is the same as that from the corresponding alcohol, trichloroethanol, in which the hydrogen is replaced by a hydroxymethyl group. Although acid yields may be changed by altering the dose rate, the relative position of the compounds if arranged in order of increasing acid yield is, in general, the same at any dose rate. Displacement of oxygen from the solutions by either nitrogen or hydrogen (Tables III and IV) lowers the acid yields but the relative position of the compounds is almost unchanged.

The carbon-halogen bond dissociation energy for the halogen-substituted methanes (Table VII) falls as the number of halogen substituents is increased and is lower for the less electronegative halogens. It is reasonable to assume that the carbon-halogen bond strength in the three groups of compounds studied, aldehydes, alcohols, and acid anions, will vary within each group in the same manner as in the substituted methanes as the number and nature of the substituting halogen atoms is changed. Thus, the greatest yields of acid are obtained on irradiation of the compounds which would be expected to have the lowest carbon-halogen bond dissociation energies, based upon the structure of the substituted methyl group present.

Chemical evidence leads to a similar conclusion; it is found that the compounds giving the greatest yield of acid on irradiation are those from which the halogen can be removed most readily by chemical reduction, and changes in halogen substitution which were found to lead to greater acid yields on irradiation also facilitate the removal of halogen by reduction. The effect of increasing halogen substitution, for example, upon the ease of reduction is shown by the action of zinc upon the chloroacetic acids (18); with this

reagent the chlorine atoms in trichloroacetic acid may be replaced one at a time by hydrogen, but each succeeding replacement requires longer or more vigorous treatment. A similar stepwise reduction of trichloroacetic acid can be achieved electrochemically by using cathodes with increasing hydrogen overpotential or by using progressively greater cathode potentials (ref. 19, pp. 47, 91). This is well illustrated by the polarography of trichloroacetic acid (Table VIII). The acid shows two waves corresponding to the removal of first one, and then a second, chlorine atom; the second wave, at the more negative half-wave potential, being the same as that obtained with dichloroacetic acid. The final chlorine could not be reduced under the conditions used though all three bromine atoms could be removed from tribromoacetic acid, the increasing half-wave potential for each succeeding step showing that reduction is progressively more difficult. The table also shows that bromine may be removed from a bromoacetic acid more readily than chlorine from the analogous chloroacetic acid.

The postulate that substituents influence the acid yield on irradiation through their effect upon the strength of the carbon-halogen bond would require the acid yield to increase with the following changes in the functional group, $-\text{COO}^- < \text{H} < -\text{CH}_2\text{OH} < -\text{CH}(\text{OH})_2 < -\text{COOH}$, in accordance with the increasing electron attraction shown by these groups, and similar to their effect on the ease of removal of halogen from a trichloromethyl group, as demonstrated by polarography (Table IX). In practice it was found that the carboxylate ion gave lower yields of acid than the alcohols and these, in turn, lower yields than the aldehydes. However, isolated irradiations of the free substituted acids have indicated that though these give higher yields than the anions they give lower yields than the alcohols and aldehydes, despite the predicted lower carbon-halogen bond strength in the acids. It seems clear that the functional group may affect the acid yield in other ways besides its indirect action upon the strength of the carbon-halogen bond. The explanation probably lies in the possibility of radical attack at either of the two carbon groups present; the susceptibility of the functional group to such attack and the nature

TABLE VII
Carbon-halogen bond dissociation energies for halogen-substituted methane (ref. 17, pp. 20, 24)

Substituted methane	Halogen substituents, R			
	F	Cl	Br	I
		kcal/mole		
$\text{H}_3\text{C}-\text{R}$	118	81	67.5	54
$\text{H}_2\text{RC}-\text{R}$		78.5	62.5	
$\text{HR}_2\text{C}-\text{R}$		73.5	55.5	
$\text{R}_3\text{C}-\text{R}$		68	49	

TABLE VIII
Half-wave potentials for the reduction of halogen-substituted acetates*

Halogen, X	XCH_2COOH	X_2CHCOOH	X_3CCOOH
		volt	
Cl	—	-1.57	-1.57
			-0.85
Br	-1.33	-1.35	-1.31
		-0.42	-0.42
I	-0.49		-0.32

*Refs. 20, 21. Saturated calomel reference electrode, pH 7.7-7.9, 25° C.

of the radical formed from it might then be more important than its indirect effect through the neighboring carbon group. The lower ratio of acid (or halide) produced to oxygen consumed as the functional group is changed from $-\text{CH}(\text{OH})_2$ to $-\text{CH}_2\text{OH}$ and $-\text{COO}^-$ (Table V) suggests that more oxygen is used up through attack at the functional group with the latter compounds. The radicals formed from the acid groups, $\text{R}\cdot\text{COO}\cdot$ and, by decarboxylation, $\text{R}\cdot$, would also be expected to be less reactive than those formed from the alcohol and aldehyde, $\text{R}\cdot\text{CHOH}$ and $\text{R}\cdot\dot{\text{C}}(\text{OH})_2$.

TABLE IX
Half-wave potentials for the reduction of the
trichloromethyl group*

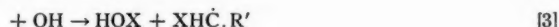
Compound	Half-wave potential, volt	Ref.
$\text{Cl}_3\text{C}\cdot\text{COOH}$	-0.45	22
$\text{Cl}_3\text{C}\cdot\text{Cl}$	-0.75	23
$\text{Cl}_3\text{C}\cdot\text{COO}^-$	-1.00	22
$\text{Cl}_3\text{C}\cdot\text{CH}(\text{OH})_2$	-1.35	24
$\text{Cl}_3\text{C}\cdot\text{CH}_2\text{OH}$	-1.45	25
$\text{Cl}_3\text{C}\cdot\text{H}$	-1.7	23

*Saturated calomel reference electrode, pH 7-8, other than $\text{Cl}_3\text{C}\cdot\text{COOH}$, 25° C.

Mechanism

The first step in the interaction of ionizing radiation and a dilute aqueous solution is the absorption of the radiation by the water to give both molecular and free radical products. For Co^{60} gamma irradiation the molecular products, hydrogen and hydrogen peroxide, are formed with G values of about 0.4 and 0.8 respectively (26); they are unreactive, compared to the free radical products, and the low concentrations produced are not likely to react directly with the organic solutes used here. The radical products are formed with higher G values, about 2.7 and 2.0 for hydrogen atoms and hydroxyl radicals respectively (26; neutral solutions), and are believed to be responsible for most of the chemical action observed.

For convenience the initial reactions between the primary radicals and the solute may be divided into attack at either the substituted methyl group or the functional group. Attack at the substituted methyl group might be as follows;



where X is a halogen atom and R' either $-\text{CH}_2\text{OH}$, $-\text{CH}(\text{OH})_2$, or $-\text{COO}^-$. A disubstituted halogen compound is shown for the purposes of illustration; this could equally be a mono- or tri-substituted group, though in the latter case reactions involving hydrogen abstraction, reactions [4] and [5], would not be possible.

Breaking of the carbon-halogen bond during the initial reactions is supported by the relationship between the strength of this bond and the yield of halide on irradiation, particularly in those cases where a chain reaction is not postulated. The removal of halogen by hydrogen atoms (reaction [2]) is analogous to the reduction of halogen compounds at a cathode and during polarography, for which hydrogen atoms have been suggested as the active intermediates (cf. ref. 19, p. 47, and ref. 27). Removal of the halogen by

hydroxyl radicals (reaction [3]) is less likely and it has been shown (15) that carbon tetrachloride does not react with chemically produced hydroxyl radicals though chloroform does, presumably by hydrogen abstraction (reaction [4]). Polarographic data (Table VIII) suggest that hydrogen atoms are more likely to abstract halogen (reaction [2]) than hydrogen (reaction [5]) unless the halogen is firmly bound.

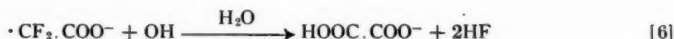
The primary inorganic radicals will also react with the functional groups present, the most probable reaction being hydrogen abstraction by the hydroxyl radicals. Most of the hydrogen atoms would be expected to react with the halogen-substituted group; polarography of the halogen-substituted aldehydes (28) shows that the halogen group is reduced in preference to the aldehyde group, both acids and alcohols are reduced less readily than the aldehydes. Hydrogen abstraction from an alcohol and an aldehyde hydrate would give the radicals $R\cdot\dot{C}HOH$ and $R\cdot\dot{C}(OH)_2$ respectively and electron transfer between an anion and a hydroxyl radical the carboxylate radical, $R\cdot COO\cdot$.

The subsequent reactions of the organic radicals are uncertain. If oxygen is not present they may combine in pairs to give stable products or react with the solute, though the yields of acid products are relatively low and the extent of the reaction must be limited. The products obtained by irradiating solutions of the substituted acetic acids appear to be similar to those formed by anodic oxidation, in which carboxylate radicals are believed to be intermediates (ref. 19, p. 97, and refs. 29, 30). For example the products formed by irradiating an aqueous solution of monochloroacetic acid in the absence of air include carbon dioxide, carbon monoxide, formaldehyde, and hydrochloric acid (14), all of which are formed at the anode when the solution is electrolyzed (31, 32); in addition glyoxylic acid was identified among the radiolysis products and small amounts of chlorine, methylene chloride, and chloromethyl chloroacetate among the electrolysis products.

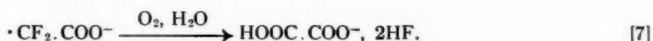
Oxygen markedly increases the yields of acid obtained on irradiation and is believed to add to the organic radicals, $R'\cdot$, to give relatively unreactive peroxy radicals, $R'O_2\cdot$, which may be unstable and break down to give a mixture of products or be converted to a more reactive alkoxy-type radical, $R'O\cdot$. The radical $R'O\cdot$ may itself be unstable and break down to give a mixture of products. The higher acid yields in the presence of oxygen can arise from the breakdown of oxygenated radicals and products to give acid materials or from the formation of reactive radicals which are able to sustain a chain reaction. The active radicals might be of the type $R'O\cdot$ or be inorganic radicals formed by the breakdown of unstable organic radicals.

Some evidence for the formation and subsequent breakdown of peroxy radicals during radiolysis arises from the formation of free fluoride from the fluorine-substituted acetates. Very little fluoride is formed from trifluoroacetate, even in the presence of oxygen (Table I), showing that the carbon-fluorine bond is not readily broken under the conditions of the irradiations. Chlorodifluoroacetate gives a greater yield of both fluoride and acid on irradiation (Table I); the yield of fluoride falls when the oxygen is absent (Table III). The carbon-fluorine bond can be broken chemically by substituting a hydroxyl group onto the carbon carrying the fluorine, when hydrolysis of the fluorine takes place in the presence of water, or by forming a free radical with the free electron on the fluorine-substituted carbon atom and allowing this to add oxygen to form a peroxy radical which will break down in the presence of water to give the fluorine as hydrogen fluoride (33). The chlorine present in chlorodifluoroacetate offers a point of attack not present in trifluoroacetate, and loss of the chlorine gives a radical which may react with either a hydroxyl radical or

oxygen and subsequently break down, i.e.,



or



The lower yield of fluoride in the absence of oxygen suggests that the changes represented by reaction [7] occur.

Iodoacetate gives a lower yield of acid (measured by $G_{\text{I}^-} + G_{\text{I}_2}$) than either monobromoacetate or monochloroacetate, though a higher yield might be expected in view of its weaker carbon-halogen bond. The concurrent formation of molecular iodine from the iodoacetate suggests that some of the initiating radicals (H and OH) are converted to less reactive iodine atoms by reaction with iodide ions or molecular iodine and so prevented from reacting with the iodoacetate. An equimolar amount of potassium iodide added to a bromal hydrate solution before irradiation prevented the formation of any acid products but gave molecular iodine with a G value of about 10. This is higher than the value for solutions of iodide alone (G_{I_2} about 1.7) and suggests that some organic radicals are formed and converted to peroxides before reaction with iodide or iodine occurs to terminate the reaction. Bromide and chloride are without effect since the chain reactions involved in the radiolysis of bromal and chloral hydrates are not hindered by the increasing concentrations of bromide and chloride ions respectively as the irradiations progress.

Organic Halogen Compounds in Dosimetry

The liberation of acid from organic halogen compounds upon irradiation has been used as the basis for methods of detecting and measuring ionizing radiation (1). The compounds most generally studied have been chloroform and tetrachloroethylene, usually in the form of the pure organic liquid overlaid with water. If a pH indicator dye is added to the aqueous layer the acid formed may be estimated visually or by means of a photoelectric colorimeter, or it may be estimated by any of the standard methods for determining strong acids. However, before the water-soluble acid can be estimated in the aqueous layer it is necessary to hydrolyze acid-precursors, generally acid chlorides, dissolved in the organic phase and extract the acid formed into the aqueous layer, a procedure that may require shaking or stirring for periods ranging from minutes to hours (cf. ref. 34). By using carefully purified materials the two-phase systems can be made sensitive to small doses of radiation of the order of 1.0 to 10 rads. The integral dose that such a system can measure is limited by the amount of oxygen present, and once this has been used up by the radiolysis reactions the yield of acid falls to a small value. Larger doses of radiation can be measured by adding small quantities of inhibitors, generally aliphatic or aromatic hydroxy compounds, which lower the amount of acid formed, and of oxygen used up, for a given dose of radiation received by the system. Exhaustion of the oxygen present still imposes an upper limit to the dose that can be measured unless steps are taken to introduce fresh oxygen while the irradiation is in progress.

The two-phase systems suffer from the disadvantage of being rather dependent upon the energy of the incident radiation. This may be largely overcome by using dilute aqueous solutions of organic halogen compounds, for example, chloral hydrate (12). The

greatest yields of acid have been obtained from aqueous solutions of chloral hydrate, bromal hydrate, and tribromoethanol; the yields shown in Table I may be increased by using more concentrated solutions (cf. refs. 3, 12) but they are generally lower than the yields from the two-phase systems. These solutions, in common with the two-phase systems, are broken down by chain reactions initiated by the radiation. The reactions are very susceptible to traces of impurities and the chain length, and hence the yield of acid is dependent on the dose rate and the temperature. These features associated with the chain reaction are undesirable in chemical dosimetry, though almost impossible to avoid, since the chain reaction itself is essential if small doses of radiation are to lead to the relatively large quantities of product that are required for a convenient determination. Among the water-soluble compounds, traces of impurity have proved particularly troublesome with bromal hydrate; chloral hydrate and tribromoethanol are available commercially for drug use and little difficulty would be expected, or has been experienced, in obtaining reproducible results with them.

If the greatest sensitivity is not required, it is possible to choose a system for which the acid yield is independent of dose rate; chloroform, in aqueous solution, is undoubtedly the first choice on the grounds of availability, ease of purification, and ease of preparation of the solution, though the acid yield is low compared to that from chloral or bromal hydrates, or the two-phase systems. Aqueous solutions have the advantage that any acid-precursors formed are hydrolyzed immediately and the acid products can be titrated to a sharp end point as soon as the irradiation is finished. In addition, chloroform has the advantage over the two-carbon compounds listed in Table I that only one acid product is formed, thus avoiding confusion that might arise between the yield of halide and the total yield of acid.

Acid formed from the non-polar compounds when they are irradiated in aqueous solution can be determined conveniently from the electrical conductivity of the solution (12, 15). By this means the acid formed can be measured continuously, at a distance, while an irradiation is in progress and the integral dose confirmed after the irradiation by titrating the acid formed.

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CYCLIALKYLATIONS OF ALKYL BENZENES WITH OLEFINS AND ALKYL HALIDES¹

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ABSTRACT

A revised mechanism is given for the formation of octamethyloctahydroanthracene from 1,3,5-tri-*t*-butylbenzene and *t*-butyl chloride. 1,3,5-Tri-*t*-butylbenzene reacts with isopropyl chloride to yield an octamethylhydrindacene which also forms when 1,3,5-triisopropylbenzene is cyclialkylated with isobutene. 1,3,5-Triisopropylbenzene is cyclialkylated with 2-methyl-2-butene to yield a decamethylhydrindacene. Treatment of 1,3,5-triisopropylbenzene with 2-chloro-2,4,4-trimethylpentane yields a hydrocarbon, C₂₃H₃₈, most probably 1,1,3-trimethyl-5,6-diisopropyl-3-neopentylindan. Structures assigned to the cyclialkylation products are based on ultraviolet, infrared, and mass spectroscopic data, and in some instances classical syntheses. Mechanisms are suggested to account for these reactions.

INTRODUCTION

In this paper, a revision is presented for a mechanism to account for cyclialkylation of 1,3,5-tri-*t*-butylbenzene with *t*-butyl chloride to form octamethyloctahydroanthracene (I). In addition, similar cyclialkylations are applied to some other systems. For example, treatment of 1,3,5-tri-*t*-butylbenzene with isopropyl chloride under Friedel-Crafts conditions yielded an octamethylhydrindacene (III). 1,3,5-Triisopropylbenzene reacted with isobutene in the presence of isopropyl chloride also to produce III. Under similar conditions, triisopropylbenzene and 2-methyl-2-butene yielded a decamethylhydrindacene (IV). Treatment of triisopropylbenzene with 2-chloro-2,4,4-trimethylpentane yielded another new compound, C₂₃H₃₈, which also was formed by cyclialkylation of triisopropylbenzene with 2,4,4-trimethyl-1-pentene in the presence of isopropyl chloride. The compound C₂₃H₃₈ apparently is 1,1,3-trimethyl-5,6-diisopropyl-3-neopentylindan (V). The structures given to the cyclialkylation products are based on ultraviolet, infrared, and mass spectroscopic data, and in some instances on classical syntheses. Mechanisms are suggested to account for the cyclialkylations.

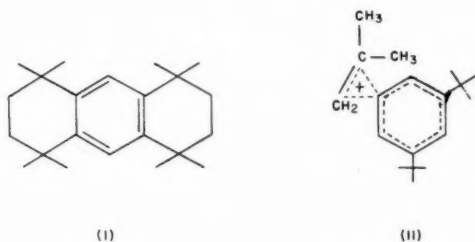
DISCUSSION

In an earlier publication (1), a mechanism was proposed for the formation of 1,1,4,4,5,5,8,8-octahydroanthracene (I) from 1,4-di-*t*- or 1,3,5-tri-*t*-butylbenzene and *t*-butyl chloride involving the formation of a primary tri-*t*-butylbenzene carbonium ion and cyclialkylation with isobutene. Condon (2) proposed an alternative mechanism for the formation of I. His mechanism requires that this cyclialkylation takes place through the 2,4,4-trimethylpentyl carbonium ion which apparently rearranges through a protonated cyclopropyl carbonium ion to the dimethylhexyl carbonium ion. It has been demonstrated by Barclay and Hilchie (3) that this dimethylhexyl system can displace *t*-butyl groups from 1,4-di-*t*-butylbenzene to produce I. However, a more adequate test of Condon's mechanism would be to carry out alkylations of aromatics with 2-chloro-2,4,4-trimethylpentane to find if the initial 2,4,4-trimethylpentyl ion rearranges to the required 2,5-dimethylhexyl system under conditions favorable for the formation of I. According to Condon's mechanism, it would be expected that I should form from benzene or the *t*-butylated benzenes and 2-chloro-2,4,4-trimethylpentane in at least as good a yield as reported (4) for the preparation of I from the *t*-butylated benzenes and *t*-butyl

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chloride. Benzene and 1,4-di-*t*-butylbenzene were therefore treated with 2-chloro-2,4,4-trimethylpentane under a variety of conditions which might be expected to cause cyclialkylation. However, no cyclialkylation products such as I could be detected in the reaction products. These negative results cannot be entirely conclusive but it does appear unlikely that this cyclialkylation proceeds via the 2,4,4-trimethylpentyl ion. The only objection to the initial mechanism proposed by Barclay and Betts (1) is that it involves a high energy primary carbonium ion. However, this neophyl ion could have a more stable bridged structure (II) where the neighboring phenyl group participates in the displacement of the hydride ion from a primary carbon.



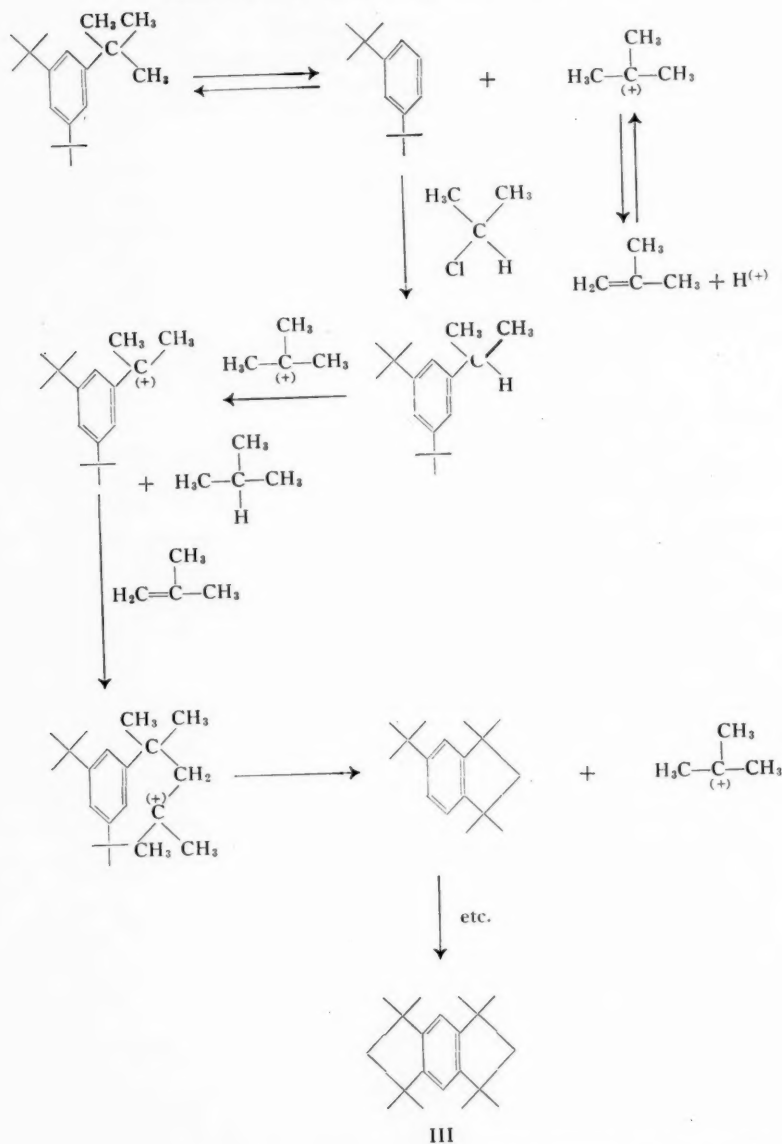
Similar cyclic bridged phenonium ions have been postulated by Cram (5) for a variety of reactions and by Schmerling and co-workers (6) to explain aluminum-chloride-catalyzed isomerizations of alkyl benzenes. Recently, Douglas and Roberts (7) postulated removal of a hydride ion from the β -carbon of propyl benzene with "anchimeric assistance from the phenyl group" to produce a phenonium ion intermediate analogous to II. In our reactions the ion II would be expected to react with isobutene at the unsubstituted CH_2 group rather than at the more hindered branched position of II and therefore I is the octamethyloctahydroanthracene which forms.

In an effort to extend these cyclialkylations to other systems, 1,3,5-tri-*t*-butylbenzene was treated with isopropyl chloride under Friedel-Crafts conditions. A compound of parent mass 270 was isolated corresponding to $\text{C}_{20}\text{H}_{30}$. This compound was dehydrogenated to yield an anthracene derivative, indicating that $\text{C}_{20}\text{H}_{30}$ is tricyclic. The infrared spectrum showed bands attributed to *t*-butyl groups and a band of 11.35 microns attributed to 1,2,4,5-tetrasubstitution. From this evidence it was proposed that this compound is 1,1,3,3,5,5,7,7-octamethylhydrindacene (III). The structure suggested for $\text{C}_{20}\text{H}_{30}$ was confirmed by a classical synthesis by the alkylation of 1,1,3,3-tetramethylindan with 2,4-dimethyl-2,4-pentanediol.

A general mechanism to account for the formation of III from 1,3,5-tri-*t*-butylbenzene and isopropyl chloride is outlined on page 96.

It is proposed that isopropyl groups replace *t*-butyl groups by a dealkylation-alkylation reaction. Then a hydride ion transfer from an isopropyl group to a *t*-butyl carbonium ion sets up a carbonium ion on a side chain which is alkylated with isobutene. The resulting cation will then cyclize with the elimination of an ortho *t*-butyl group. The remaining *t*-butyl group is replaced by isopropyl which in turn is cyclialkylated so that III is the final product. This interpretation is supported by the fact that 1,3,5-triisopropylbenzene is cyclialkylated with isobutene in the presence of isopropyl chloride (as a hydride ion acceptor) to give a good yield of III.

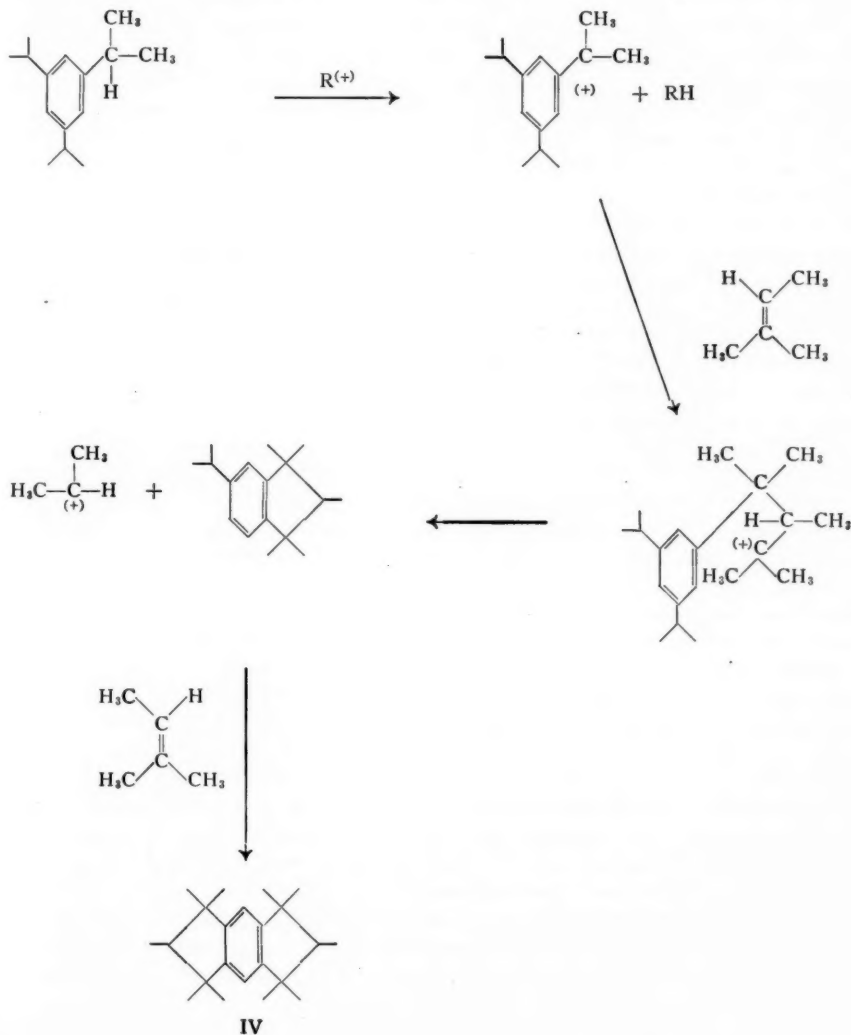
The mechanism for the formation of III might also be described by the condensation of isobutene and an isopropyl cation to form the 2,4-dimethylpentyl carbon skeleton.



The latter could possibly replace isopropyl or *t*-butyl groups and form III. However, attempts to prepare III in this way by the alkylation of 1,4-di-*t*-butylbenzene with 2-chloro-2,4-dimethylpentane failed. It is therefore unlikely that the reaction proceeds by this alternative mechanism.

The formation of polymethylhydrindacenes was extended to another system by cyclialkylating 1,3,5-triisopropylbenzene with 2-methyl-2-butene in the presence of isopropyl chloride. In this case a high melting (245–245.6°) hydrocarbon ($\text{C}_{22}\text{H}_{34}$) was

obtained with an ultraviolet spectrum practically identical with that of III. The infrared spectra of these hydrocarbons were also very similar. Both had bands at 7.75, 8.10, and near 8.5 microns attributed to *t*-butyl groups. The main difference was due to bands appearing in the spectrum of the higher melting sample at 8.9 microns and in the 9.4- to 10-micron region which were absent in III. Both compounds had a strong band at 11.35 microns attributed to 1,2,4,5-tetrasubstitution. Therefore, the higher melting compound most probably has the decamethylhydrindacene structure IV and would form from 1,3,5-triisopropylbenzene as follows.



The cyclialkylations outlined above have some similarity to the reaction discovered by Ipatieff, Pines, and Olberg (8) for the formation of 1,3,3,6-tetramethyl-1-*p*-tolylindan

from *p*-cymene and a number of different olefins in the presence of sulphuric acid or hydrogen fluoride. Schlatter also reported similar reactions in the formation of 1,1,3,3,5-pentamethylindan by the *t*-butylation of *p*-cymene (9) and of the side product 1,1,3,3,5,6-hexamethylindan from the alkylation of 1,2-dimethyl-4-*t*-butylbenzene (10). All of these cyclialkylations illustrate how highly branched, condensed ring systems can be produced in essentially a one-step process from relatively simple starting materials. The so-called classical syntheses of these hydrocarbons on the other hand often involve many steps which often proceed in poor yields. That these processes must have practical significance is evident in some recent patents (11, 12, 13) on the production of polyalkyl indans from styrene compounds. Many of these branched hydrocarbons are of practical importance to the perfume industry and the petroleum industry.

Although 2-chloro-2,4,4-trimethylpentane failed to cyclialkylate benzene or 1,4-di-*t*-butylbenzene, it reacted with 1,3,5-triisopropylbenzene to give an interesting unexpected result. A crystalline product was isolated from which two compounds were separated. The main component was a compound of m.p. 101–102° (V). A small amount of another compound, m.p. 203–205° (VI), was also separated.

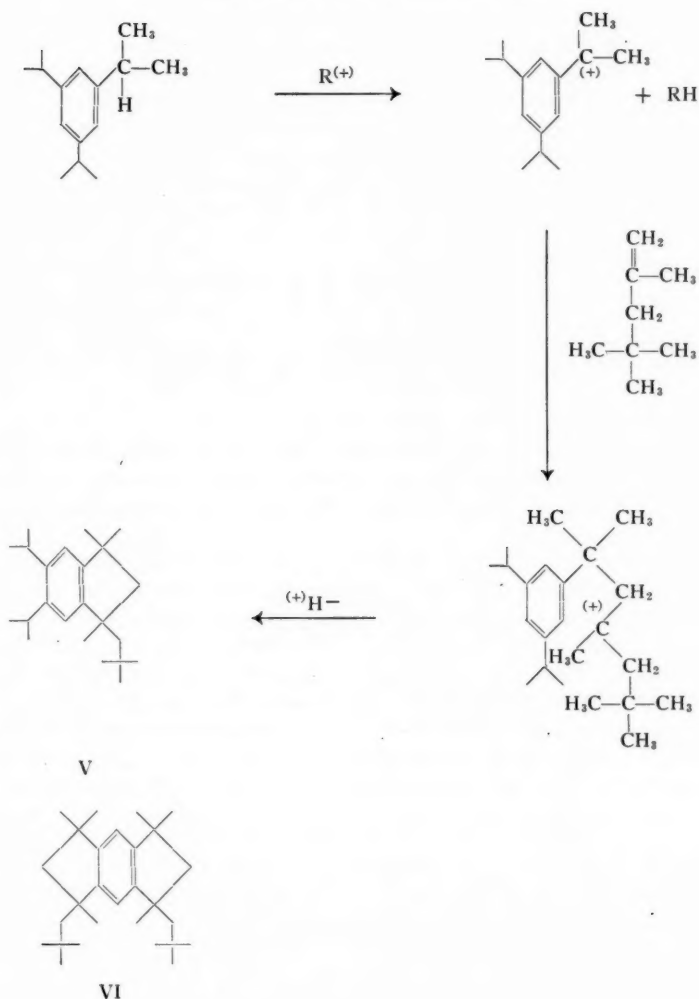
The mass spectrum analysis of V showed that it consists mainly of a compound of mass 314. There was also a large peak at mass 243 which corresponds to a loss of C_6H_{11} from the compound of mass 314. The infrared spectrum of V showed bands attributed to isopropyl groups and to tetrasubstitution. Dehydrogenation of this compound in a sealed tube at a high temperature yielded a product whose ultraviolet spectrum indicated the presence of a substituted naphthalene.

Although VI was not available in sufficient amount for a complete analysis, the mass spectrum indicated a parent mass of 383 and a peak at mass 311 corresponded to the loss of a C_6H_{11} group from a compound of mass 383. The ultraviolet spectrum of VI was practically identical with that of octamethylhydrindacene indicating that VI is most probably a similar polyalkyl hydrindacene.

The structures shown on page 99 for V and VI seem logical to explain the analyses discussed above. Reaction mechanisms are illustrated to account for the formation of these compounds.

In the reactions outlined on page 99 the olefin involved in the cyclialkylation is 2,4,4-trimethyl-1-pentene since only this isomer would lead to structures V and VI which lose a neopentyl fragment during the mass spectroscopic analysis. This olefin is not the expected one according to the classical Saytzeff rule by which the proton is expected to be eliminated from the CH_2 group to form 2,4,4-trimethyl-2-pentene. However, Whitmore and Rohrmann (14) have found that the corresponding alcohol, dimethyl-neopentylcarbinol, dehydrates to yield 2,4,4-trimethyl-1-pentene. In both cases the neopentyl group does not take part in the elimination. Both of these "unusual" eliminations can be explained if one assumes that the factor governing the course of elimination here is inhibition of close approach of a proton acceptor to the hindered CH_2 group.

The 1,2,4,5-formulation for V makes it possible to offer an explanation of why this dicyclic compound forms in better yields than the tricyclic compound, VI. Usually in these cyclialkylation experiments the tricyclic compound forms very readily and it is difficult to isolate dicyclic compounds analogous to V. However, further cyclialkylation of V in this case would not readily take place because the bulky olefin (trimethyl-1-pentene) would be hindered from alkylating an isopropyl group by an adjacent isopropyl group. The 1,2,4,5-orientation for V is also favored by its ultraviolet spectrum which is very similar to the spectrum of 1,2,4,5-tetraisopropylbenzene. The latter showed bands



at λ_{\max} 2770 Å, $\epsilon = 649$ and λ_{\max} 2682 Å, $\epsilon = 586$, while V had bands at λ_{\max} 2760 Å, $\epsilon = 749$ and λ_{\max} 2677 Å, $\epsilon = 690$.

As a check for the structure suggested for V and the mechanism involving the postulated olefin 2,4,4-trimethyl-1-pentene, experiments were carried out on the alkylation of 1,3,5-triisopropylbenzene with this olefin in the presence of isopropyl chloride. This reaction did produce a compound identical with V and in high yield.

EXPERIMENTAL

The melting points were obtained with a Fisher-Johns apparatus equipped with a microscope, and are uncorrected. Ultraviolet spectra were recorded on a Beckman DK-2 ratio recording spectrophotometer using spectro-grade cyclohexane as the solvent.

The infrared spectra were recorded on a Perkin-Elmer Model 137 instrument using purified carbon disulphide as the solvent. Some of the infrared spectra were determined by an independent laboratory. The mass spectroscopic measurements were made in another laboratory on a special high temperature inlet mass spectrometer. The ultimate analyses were determined by the Schwarzkopf Microanalytical Laboratory, New York.

In all of the cyclialkylation experiments the progress of the reactions was followed by means of the recording ultraviolet spectrophotometer. Aliquots were taken from the reaction mixtures at short time intervals, the aluminum chloride complexes decomposed in water, and spectra were recorded immediately. In this way the course of the reaction was followed with a time lag of not more than a few minutes. Significant changes, such as changes in positions of alkyl groups on the benzene ring, the formation of di- or tri-cyclic products, and in some instances the introduction of a conjugated double bond were quite easily detected. Thus the reaction could be terminated at an appropriate time to permit isolation of the desired products or intermediates.

*The Reaction of 1,3,5-Tri-*t*-butylbenzene with Isopropyl Chloride*

Isopropyl chloride was prepared almost quantitatively by heating isopropyl alcohol with an equal volume of a saturated solution of zinc chloride in concentrated hydrochloric acid while passing through hydrogen chloride. The product was distilled off the top of a reflux condenser on formation.

1,3,5-Tri-*t*-butylbenzene, prepared as described by Barclay and Betts (4), (6.6 g, 0.027 mole) and isopropyl chloride (5.8 g, 0.074 mole) were stirred together and cooled to below 0°. Nine grams of aluminum chloride (0.067 mole) was added in small portions over a period of 2 hours. After 7 hours reaction time, the brown complex which formed was decomposed in cold water. A white solid (4.6 g) was formed which was filtered and recrystallized from ethanol-benzene. After five recrystallizations the melting point was 220–222.5°. Calc. for $C_{26}H_{30}$: C, 88.84; H, 11.16; molecular weight, 270. Found: C, 88.53, 88.64, 88.61, 88.96; H, 11.04, 11.10, 10.78, 11.04.

This compound showed a peak in the mass spectrometer corresponding to a parent mass of 270. There was also a large peak at 255 attributed to the loss of a methyl fragment.

The infrared spectrum of this compound, both in carbon disulphide solution and in potassium bromide pellets, showed a series of bands in the 1200- to 1500-cm⁻¹ region attributed to *t*-butyl groups. In the ultraviolet spectrum there were bands at λ_{\max} 2810 Å, $\epsilon = 4725$; λ_{\max} 2760 Å, $\epsilon = 4243$; λ_{\max} 2715 Å, $\epsilon = 3760$; and λ_{\max} 2670 Å, $\epsilon = 2700$.

This compound was dehydrogenated by heating 1 g of it with 2 g of selenium powder in a sealed tube for 40 hours at 400°. The product fluoresced under an ultraviolet light. The ultraviolet spectrum indicated that it is a substituted anthracene.

A solution of 0.55 g of this hydrocarbon in a mixture of 25 ml of glacial acetic acid and 15 ml of acetic anhydride was treated with 1 ml of fuming nitric acid and heated at 70° for 3 hours. Distillation of the solvent mixture left a crude nitro derivative which was contaminated with some unreacted hydrocarbon. Repeated recrystallizations from acetone yielded colorless crystals, m.p. 275–277°.

Cyclialkylation of 1,3,5-Triisopropylbenzene with Isobutene

Isobutene was generated by dropping 85% phosphoric acid on warm *t*-butyl alcohol. The gas thus produced was passed through an ice trap, a bubbler containing 85% phosphoric acid, and a calcium chloride tube. This was then bubbled into the reaction mixture which contained 12.5 g of 1,3,5-triisopropylbenzene, prepared as described by

Gustavson (15), 9.6 g of isopropyl chloride (0.122 mole) as a hydrogen acceptor, and 16.3 g of aluminum chloride (0.122 mole). The reaction was cooled to below 0° in an ice-salt bath and the gas was allowed to pass through for $5\frac{1}{2}$ hours. The reaction was decomposed on water and allowed to stand overnight. The organic material was extracted with ether. The ether was distilled off and the residue recrystallized from ethanol-benzene. A solid was obtained which weighed 9.8 g (59% yield). After five recrystallizations the melting point was $218-220^{\circ}$. The melting point was not lowered when the product was mixed with the product of alkylation of 1,3,5-tri-*t*-butylbenzene with isopropyl chloride.

Synthesis of 1,1,3,3,5,5,7,7-Octamethylhydrindacene (II)

1,1,3,3-Tetramethylindane was prepared, as described by Bogert and Davidson (16), starting with diacetone alcohol and benzene. Diacetone alcohol was prepared as described in ref. 17. 2,4-Dimethyl-2,4-pentanediol was prepared as described by Franke and Kohn (18) from diacetone alcohol and methyl magnesium iodide.

The indane (1.24 g, 0.007 mole) and the diol (0.94 g, 0.007 mole) were dissolved in 4 ml of carbon disulphide. Aluminum chloride (0.95 g, 0.007 mole) was added in small portions over a period of $\frac{1}{2}$ hour. A complex began to form almost immediately after the addition of aluminum chloride. The mixture was stirred for 15 minutes, and then another 0.95 g of aluminum chloride was added slowly. The reaction was allowed to proceed for a total of 4 hours. It was then poured into water and the organic material was extracted with ether. On concentration of the ether, 1.75 g (88% yield) of crude crystals was obtained. These crystals were purified by recrystallization from ethanol-benzene three times to yield a material of m.p. $218.5-220^{\circ}$.

The melting point of the synthetic hydrindacene did not lower when mixed with the product of the cyclialkylation reactions described in previous sections. The ultraviolet absorption spectrum of the synthetic compound, II, was identical with the spectrum of the cyclialkylation product. The X-ray diffraction patterns of the synthetic product and the cyclialkylation product were also identical.

Cyclialkylation of 1,3,5-Triisopropylbenzene with 2-Methyl-2-butene

Isopropyl chloride (5.0 g, 0.05 mole) was cooled to -5° in a three-neck flask. Then aluminum chloride (3.33 g, 0.025 mole), and a mixture of 2-methyl-2-butene (4.0 g, 0.05 mole) and 1,3,5-triisopropylbenzene (5.0 g, 0.025 mole), were added slowly to the cooled reaction mixture. At the end of 4 hours, the reaction mixture was decomposed in cold water and allowed to stand overnight. The semisolid hydrocarbon layer was filtered to yield 4 g of crude product. Four recrystallizations from ethanol-benzene produced colorless crystals, m.p. $245-245.6^{\circ}$. Calc. for $C_{22}H_{34}$: C, 88.51; H, 11.49. Found: C, 88.10, 87.96; H, 11.08, 11.24. In the mass spectroscopy, this compound showed a parent mass of 298 corresponding to $C_{22}H_{34}$.

The ultraviolet spectrum of this material had bands at λ_{\max} 2800 Å, $\epsilon = 4760$; λ_{\max} 2747 Å, $\epsilon = 4170$; λ_{\max} 2705 Å, $\epsilon = 3680$; λ_{\max} 2660, $\epsilon = 2680$.

The Reaction of 1,3,5-Triisopropylbenzene with 2-Chloro-2,4,4-trimethylpentane

1,3,5-Triisopropylbenzene (5.2 g, 0.025 mole) and 2-chloro-2,4,4-trimethylpentane (7.5 g, 0.050 mole) were placed in a three-neck flask and cooled to below 0° in an ice-salt bath. Aluminum chloride (6.7 g, 0.050 mole) was added in small portions with stirring over a period of $1\frac{1}{2}$ hours. After 8 hours reaction time, the reaction mixture was poured into water and allowed to stand overnight. The solid material which separated was

filtered and recrystallized from benzene-ethanol. Forty milligrams of a compound with a melting point of 203–205° separated out in the first crop of crystals. The melting point of this compound was lowered when mixed with octamethyloctahydroanthracene (I) or when mixed with octamethylhydrindacene (III). The ultraviolet spectrum of the compound of m.p. 203–205° showed maxima at the same wavelengths as observed for III. In the mass spectrometer this compound showed a parent mass of 383 with a peak at mass 311 corresponding to the loss of a C_5H_{11} fragment.

On concentration of the original benzene-ethanol solution, 1.2 g of a second compound with m.p. 101–102° separated. Calc. for $C_{23}H_{38}$: C, 87.82; H, 12.18; molecular weight, 314. Found: C, 88.44, 88.53; H, 11.87, 11.88.

The mass spectrum of the lower melting compound showed a parent mass of 314. There was also a large peak at mass 243, corresponding to the loss of a C_5H_{11} fragment. The infrared spectrum of this compound in a potassium bromide pellet showed two strong bands of equal intensity at 7.28 and 7.37 microns attributed to isopropyl groups. There was also a strong band at 11.45 microns attributed to 1,2,4,5-tetrasubstitution. The ultraviolet spectrum of this compound showed bands at λ_{max} 2760 Å, $\epsilon = 749$ and λ_{max} 2677 Å, $\epsilon = 690$.

A sample of the compound of m.p. 101–102° (0.2 g) was dehydrogenated by heating with an equal weight of selenium powder in a sealed tube at 320° for 10 hours. The crude product was dissolved in cyclohexane and chromatographed on alumina using cyclohexane as eluant. The chromatograph fractions all showed a strong band in the ultraviolet spectrum at 2280 Å with weak absorption in the 2800 Å region containing some fine structure much like the alkyl naphthalenes.

Cyclalkylation of 1,3,5-Triisopropylbenzene with 2,4,4-Trimethyl-1-pentene

The 2,4,4-trimethyl-1-pentene used in these experiments was obtained from Matheson, Coleman and Bell, East Rutherford, N.J. It was also prepared by fractionating diisobutylene (η_D^{20} 1.4102) in a Podbielniak column. The diisobutylene was prepared by the procedure of Whitmore and co-workers (19). The 2,4,4-trimethyl-1-pentene isomer was removed in the fraction which boiled at 101° (760 mm), η_D^{20} 1.4090. The literature values (19) are 101.2° (760 mm) and η_D^{20} 1.4082.

1,3,5-Triisopropylbenzene (10 g, 0.05 mole) was dissolved in 25 ml of carbon disulphide and cooled in an ice-salt bath to -10° . A mixture of isopropyl chloride (5.6 g, 0.06 mole) and 2,4,4-trimethyl-1-pentene (5.6 g, 0.05 mole) was slowly added to the cooled, stirred solution over a period of 2 hours. Aluminum chloride (1.5 g, 0.01 mole) was added in small portions over the same period. From ultraviolet spectra run on various aliquots, the reaction product appeared to be formed in high yield after approximately 1 hour. After 2 hours reaction time, the carbon disulphide layer was poured into crushed ice and the organic layer extracted with ether. In concentrations of the ether extract, there was obtained 2 g of crystals and 5 g of semisolid material. The latter showed approximately the same ultraviolet spectrum as the crystalline material. The crude material was recrystallized from ethanol to yield colorless needles, m.p. 105–106.5°. This product was found to be identical with the product from alkylation of 1,3,5-triisopropylbenzene with 2-chloro-2,4,4-trimethylpentane by mixed melting points and ultraviolet spectra.

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THE PHOTOLYSIS AND THE FLUORESCENCE OF PERFLUORO DIETHYL KETONE¹

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ABSTRACT

The photolysis and the fluorescence of $C_2F_5COC_2F_5$ have been studied at various temperatures, concentrations, and wavelengths. There is a strong dependence of the photochemical yield and to a lesser extent of the relative fluorescence yield on these factors. The reaction products are solely CO and C_4F_{10} . The fluorescence is excited by light of the wavelength region between 2537 Å and 3650 Å. The fluorescence band lies in almost the same wavelength region as that of CF_3COCF_3 and the relative fluorescence yield is slightly less in the higher concentration region. This behavior closely follows the pattern for CF_3COCF_3 and, hence, may be discussed by the same mechanism. A comparison is made of the primary photochemical reaction among fluorinated ketones.

INTRODUCTION

The photolyses of CF_3COCF_3 (1) and $C_3F_7COC_3F_7$ (2) have been investigated earlier in this laboratory. It was found that the dissociation takes place via an electronically excited species and that CO and fluorocarbons, formed by recombination of CF_3 and C_3F_7 radicals, are the sole products. The primary photochemical yield can be obtained directly from the rate of CO formation.

The fluorescence efficiency of CF_3COCF_3 has been studied in connection with the photolysis and a mechanism of the primary process has been presented (3, 4). Fluorescence has been observed also during the photolysis of $C_3F_7COC_3F_7$ but to such a small extent that no measurements have yet been made (unpublished observation by H. Okabe). In view of the simplicity of the mechanism it seems of interest to extend the investigation to other fluorinated ketones. The main purpose of this work is to study the photolysis and the fluorescence of $C_2F_5COC_2F_5$ and to see if the proposed mechanism (4) can be applied to this compound.

EXPERIMENTAL

The apparatus and experimental procedure have already been described (2, 3, 4). The quartz reaction cells used were 10 cm in length for photolysis and 15 cm for fluorescence experiments. The light source was a Hanovia S-500 lamp operated on a regulated supply. Radiation of 2640 Å was isolated for the photolysis experiments by means of a Corning 9863 filter and 5 cm of chlorine (100 mm Hg). The transparency band of this combination has a maximum at 2640 Å. Light in the 2537 Å region is also transmitted but is negligibly absorbed by the ketone. The $C_2F_5COC_2F_5$ was supplied by Dr. Leitch of this laboratory and later by Merck and Co. of Canada. The ketone was carefully distilled on a Podbielniak column (b.p. 26° C) and dried on P_2O_5 . It was then degassed by bulb-to-bulb distillation under vacuum. A typical mass spectrometric cracking pattern is shown in Table I. Samples supplied for the early stages of this work showed the same mass spectro-

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TABLE I
 Mass spectrum of $C_2F_5COC_2F_5^*$

Mass number	Rel. height	Probable positive ion	Mass number	Rel. height	Probable positive ion
197	0.38	$C_2F_5COCF_2$	97	1.75	†
193	0.26	C_3F_8	93	3.14	C_3F_3
181	0.29	C_4F_7	85	0.5-2.5	† (from SiF_4)
162	0.28	C_4F_6	81	3.80	C_2F_3
149	0.29	†	78	4.73	CF_2CO
147	100	C_2F_5CO	74	0.64	C_3F_2
144	0.76	†	71	0.69	†
131	1.49	C_3F_6	69	130	CF_3
128	3.40	C_2F_4CO	62	0.77	C_2F_2
124	0.42	C_4F_4	50	10.2	CF_2
119	284	C_3F_3	47	0.34	†
112	0.60	C_3F_4	44	1.20	†
109	4.00	C_2F_3CO	31	20.0	CF
100	22.9	C_2F_4	28	9.0	CO

*The isotope peaks are not recorded.

†These peaks are not attributed. They are usually found in mass spectra of fluorinated hydrocarbons (see N.B.S. Reports).

graph except for relative amounts of trace impurities. Later samples contained significant quantities of benzene and some unidentified bromine compound. These were removed by partition chromatography using a fluoroester column (Fluid 316, Fluoroester Lubricant, Petroleum Chemicals Division, E.I. DuPont De Nemours and Co., 30% by weight on Fisher Scientific Company Columpak) maintained at -15°C . On a 200-cm column, 10 mm i.d., with a hydrogen flow rate of 120 cc/min the appearance time of the ketone was 17 minutes.

Following photolysis runs, carbon monoxide was pumped from the products at -210°C . The unreacted ketone and other photolysis products were collected together owing to the impossibility of a separation by low temperature distillation. In the later stages of the photolysis work the condensable products were analyzed by gas chromatography using a 3-foot alumina column (80-100 mesh) at 25°C . The ketone appears to be completely adsorbed by the column. The retention volume of C_4F_{10} is about 600 cc but this varies considerably with the amount of ketone on the column and with the moisture content of the alumina used. All quantum yields were determined using acetone as an actinometer.

The fluorescence spectrum was taken with a Hilger intermediate quartz spectrograph on a Kodak 103_a-B plate. The relative fluorescence yield, Q , in arbitrary units, is obtained from the following equation (4).

$$Q = \frac{D_t - D_t^0}{D_t^0 - D_t} \frac{S_t T}{\lambda_t}$$

where D_t is the galvanometer deflection for the fluorescence light emerging from the center of the cell, D_t^0 is the deflection for scattered light from the empty cell, D_t and D_t^0 are the deflection for the transmitted light with and without the gas in the cell respectively, S_t is the spectral sensitivity of the phototube to the transmitted light of wavelength λ , and T is the % transmission of an exit window. This equation is approximately valid when the absorption of the gas is not large.

RESULTS

The absorption spectrum was recorded with a Cary spectrometer. The spectrum

extends over a wavelength region between 2500 Å and 3600 Å. Some structure is observed between 3000 Å and 3500 Å. The molar extinction coefficient, k , in $\text{l. mole}^{-1} \text{cm}^{-1}$ is shown in Table II.

TABLE II
The molar extinction coefficient, k , ($\text{l. mole}^{-1} \text{cm}^{-1}$) of $\text{C}_2\text{F}_5\text{COCF}_3$ at various wavelengths

Wavelength (Å)	k at 23° C
2640	3.50
3130	22.3
3340	14.3

The coefficient at 3130 Å is about three times as large as that of CF_3COCF_3 .

Photolysis

The results of runs in which the condensable products were analyzed by adsorption chromatography are shown in Table III. Within experimental error the quantum yields based on CO and on C_4F_{10} are identical. Hence CO and C_4F_{10} would appear to be the sole products of the photolysis. As an additional check runs have been performed at room temperature up to 50% decomposition and the products, after elimination of CO, analyzed on the mass spectrometer. The peak at mass 147 was used for the ketone and peaks at masses 150 and 169 for C_4F_{10} . The total spectrum was that predictable from the sum of the two pure samples except for very minor discrepancies (for instance the ratio 150/169 was slightly altered in the presence of the ketone). The quantity of C_4F_{10} was equal within 5% to the CO produced. No peaks attributable to other products were noticed. Furthermore, the total number of moles of gas collected from the cell after the long runs was always found, after removal of CO, to be equal to the initial number of moles of ketone introduced. All this is in agreement with the exclusive formation of CO and C_4F_{10} .

The primary photochemical yield, based on the rate of CO production, was measured at various temperatures, concentrations, and wavelengths. Figure 1 illustrates quantum yield vs. concentration at four temperatures. Light of wavelength 3130 Å was used for

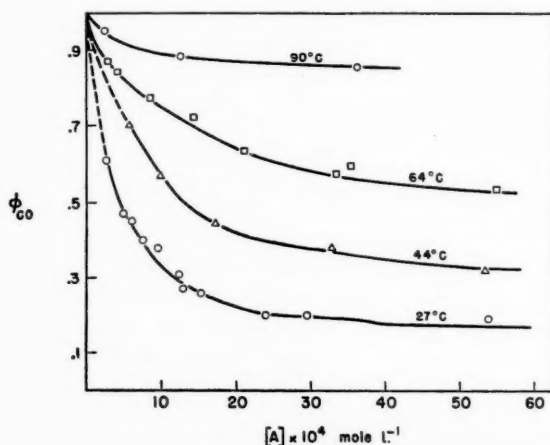


FIG. 1. The photochemical yield at various temperatures vs. concentration at 3130 Å.

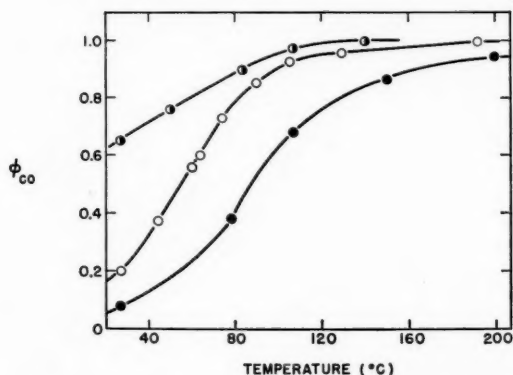


FIG. 2. The effect of temperature on quantum yield for production of carbon monoxide; ○ perfluoro di-*n*-propyl ketone, ◐ perfluoro diethyl ketone, ● hexafluoroacetone. Concentration approximately 26×10^{-4} mole l^{-1} , $\lambda = 3130 \text{ \AA}$.

excitation. Figure 2 shows the quantum yield as a function of temperature. The points shown are taken in part from Fig. 1 at a concentration of 26×10^{-4} mole l^{-1} , additional points being obtained from runs at other temperatures using approximately this concentration. The curves for perfluoro di-*n*-propyl ketone and hexafluoroacetone under similar conditions are included for comparison. Figure 3 shows quantum yield as a

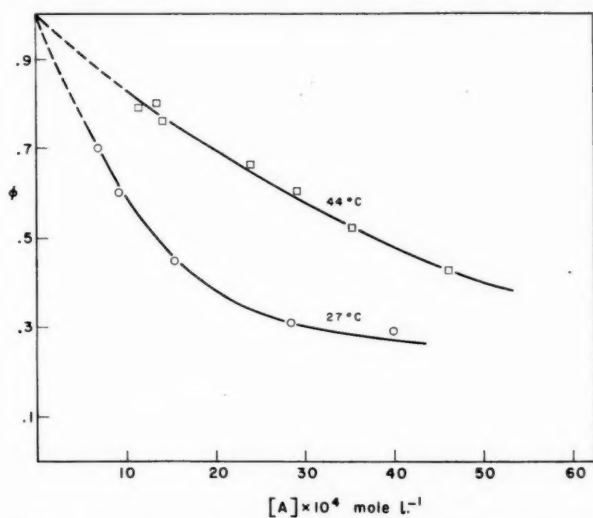


FIG. 3. The photochemical yield at various temperatures vs. concentration at 2640 \AA .

function of concentration at two different temperatures when light of 2640 \AA was used for excitation.

Fluorescence

The fluorescence is observed with light of any wavelength between 2537 \AA and

TABLE III
A comparison of quantum yields based on carbon monoxide and on perfluorobutane

Temp. (° C)	Concentration (10^{-4} mole/l.)	ϕ_{CO}	$\phi_{\text{C}_4\text{F}_{10}}$
192	8.1	1.00	0.99
106	26.7	0.93	0.93
90	33.1	0.85	0.84
	12.4	0.87	0.85
74	27.8	0.73	0.73
60	26.0	0.56	0.57

3650 Å. The fluorescence band extends over the wavelength region between 3500 Å and 5000 Å with a broad maximum at about 4100 Å. There is little effect of temperature on the position and the apparent intensity distribution of the band.

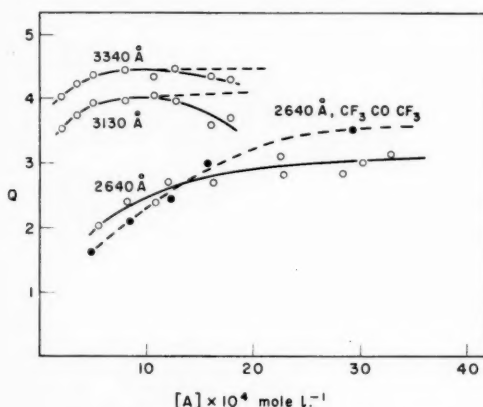


FIG. 4. The relative fluorescence yield at various wavelengths vs. concentration at room temperature; the curves are those of $\text{C}_2\text{F}_5\text{COC}_2\text{F}_5$ unless otherwise noted.

Figure 4 shows the concentration dependence at room temperature of Q at various wavelengths. For comparison Q for CF_3COCF_3 at 2640 Å is added. The apparent decrease of Q beyond the concentration of 10×10^{-4} moles per l. at 3130 Å and 3340 Å is undoubtedly due to the invalidity of the equation used in its calculation, which holds only when the absorption is less than 50%. The temperature dependence of the fluorescence yield was measured over the range from room temperature to 190° C. The fluorescence yield decreases with an increase of temperature with a negative temperature coefficient of about 0.7 kcal per mole, when light of 3130 Å and a concentration of 52×10^{-4} mole per l. are used.

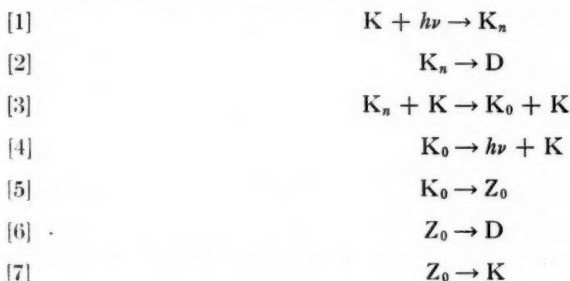
DISCUSSION

The photochemical and the fluorescence behavior of $\text{C}_2\text{F}_5\text{COC}_2\text{F}_5$ as a function of temperature, concentration, and wavelength closely resembles that of CF_3COCF_3 , namely:

(1) The mechanism of the photolysis is obviously the general one accepted for the other fluorinated ketones.

(2) The photochemical yield, ϕ , increases and approaches unity as the concentration decreases. It increases with an increase of temperature and excitation energy. The yield has a larger concentration dependence at shorter wavelength over the moderate (10×10^{-4} mole per l.) and higher concentration range at the same temperature (Figs. 1 and 3).

(3) The fluorescence band extends over almost the same wavelength region. The relative fluorescence yield increases with an increase of concentration and with a decrease of excitation energy, approaching almost 70% that of CF_3COCF_3 . The increase is larger at shorter wavelength (Fig. 4). The yield decreases as the temperature increases and the negative temperature coefficient is of the same order of magnitude. The mechanism may therefore be expressed by equations previously proposed (4).



where K , K_n , and K_0 designate the ground electronic state of $\text{C}_2\text{F}_5\text{COC}_2\text{F}_5$ and the n th and 0th vibrational levels of a singlet excited state from which the fluorescence originates. D denotes the dissociation products; Z_0 represents a molecule in the lowest vibrational level of another excited (probably triplet) state, from which dissociation and possibly internal conversion take place but not emission. From the above mechanism, the following equation is obtained:

$$[8] \quad \frac{\phi}{1-\phi} = \frac{\alpha}{1-\alpha} + \frac{k_2}{k_3[K](1-\alpha)}$$

where α is the photochemical yield at infinite concentration. Figure 5 shows the relationship between $\phi/(1-\phi)$ and the reciprocal of the concentration at various temperatures and wavelengths. The data fit the equation well at 3130 Å, whereas at 2640 Å the equation is obeyed only approximately. In Fig. 5 the data at 3130 Å enable a reliable extrapolation to be made to $1/[A] = 0$, and hence the intercepts can be established with some certainty. Unfortunately, since the lines at 2640 Å are curved it is impossible to establish the value of the intercepts with any degree of certainty. The mechanism suggests that the intercepts should have the same values at both wavelengths, and the curves have been drawn in this way. It should be emphasized, however, that while the data are entirely consistent with common intercepts, they do not in any way establish this point. The rate of dissociation from upper vibrational levels of the singlet excited state, k_2 , obtained from the slopes, is larger at the shorter wavelength. The values of α obtained from the intercept are given in Table IV. For comparison, α for $\text{CF}_3\text{COC}_3\text{F}$ and $\text{C}_3\text{F}_7\text{COC}_3\text{F}_7$ are also given.

As can be seen from Table IV, α at the same temperature increases in the order CF_3COCF_3 , $\text{C}_2\text{F}_5\text{COC}_2\text{F}_5$, $\text{C}_3\text{F}_7\text{COC}_3\text{F}_7$. If a plot is made of $\log \{(1/\alpha) - 1\}$ vs. $1/T$ for

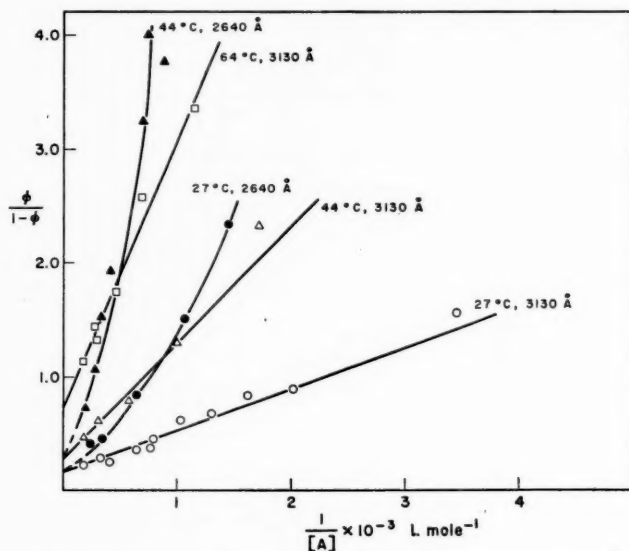


FIG. 5. The relationship between $\phi/(1-\phi)$ and the reciprocal of concentration at various temperatures and wavelengths.

TABLE IV

The photochemical yield at infinite concentration, α , at various temperatures for fluorinated ketones at 3130 Å

Compound	Temperature (°C)	α
$C_2F_5COC_2F_5$	27	0.15
	44	0.27
	64	0.43
	90	0.83
$CF_3COCF_3^*$	27	0.04
	53	0.18
	78	0.37
	107	0.63
	219	1.0
$C_3F_7COC_3F_7^\dagger$	27	0.55
	50	0.78
	80	0.90
	107	1.0

*Reference 1. †Reference 2.

these compounds, apparent negative activation energies of 9.2, 8.9, and 7.8 kcal per mole are obtained for CF_3COCF_3 , $C_2F_5COC_2F_5$, and $C_3F_7COC_3F_7$ respectively. If the mechanism is correct these energies correspond approximately to the activation energy differences between the dissociation and the internal conversion from the (triplet) state.

If a comparison is made of the photolysis at 27° C between $C_2F_5COC_2F_5$ and CF_3COCF_3 at 2640 Å, where the dissociation would mainly originate from higher vibrational levels, it is evident that ϕ for $C_2F_5COC_2F_5$ is smaller in the lower concentration region, but larger at higher concentrations. In other words, ϕ for $C_2F_5COC_2F_5$ has a smaller con-

centration dependence at this wavelength. From equation [8] this gives for $C_2F_5COC_2F_5$ a value of k_2/k_3 less than half that for CF_3COCF_3 . Assuming the same rate of deactivation for both compounds, k_2 is much smaller in $C_2F_5COC_2F_5$. This suggests that since there are more vibrational degrees of freedom for $C_2F_5COC_2F_5$, there will be less probability that the energy will concentrate in the particular bond leading to dissociation.

Corresponding to the smaller concentration dependence of ϕ for $C_2F_5COC_2F_5$ at $27^\circ C$ and 2640 \AA , there is also less concentration dependence of Q at this temperature and wavelength (Fig. 4). It would be of great interest to find direct evidence of the two close-lying excited states of these molecules. It is possible that ultraviolet spectroscopy, performed under conditions such that no dissociation would occur (low temperature and moderate pressures), may supply the answer.

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THE POLYSACCHARIDES OF *FURCELLARIA FASTIGIATA*

I. ISOLATION AND PARTIAL MERCAPTOLYSIS OF A GEL-FRACTION¹

T. J. PAINTER

ABSTRACT

Addition of potassium chloride to an aqueous extract of the red alga *Furcellaria fastigiata* precipitated a polysaccharide containing residues of D-galactose and 3,6-anhydro-D-galactose in the approximate ratio 1.3:1. Approximately two monomer units in five bore sulphate half-ester groups. The fraction gave a single, sharp peak in the analytical ultracentrifuge. Partial mercaptolysis afforded the crystalline diethyl mercaptals of D-galactose, 3,6-anhydro-D-galactose, and 4-O-β-D-galactopyranosyl-3,6-anhydro-D-galactose (A); the respective yields were 27%, 20%, and 42% w/w of the recovered mercaptolysate. The polysaccharide resembles κ-carrageenin.

The red alga *Furcellaria fastigiata* (Huds.) Lamour. contains a hydrocolloid which is similar in properties to carrageenin (1, 2). The alga grows in the Baltic Sea, and is particularly abundant in the adjacent Kattegatt, where it is harvested for the manufacture of "Danish agar", or "furcellaran" (3). It is also reported to grow in the Gulf of St. Lawrence, Canada (4), in commercial quantities (5).

In 1943, Kylin showed that residues of D-galactose, and sulphate half-ester groups were present in the mucilage (6). More recently, Dillon, O'Colla, and co-workers found that residues of 3,6-anhydro-galactose were also present (7). The unfractionated mucilage was subjected to acetylative desulphation; examination of the degraded, sulphate-free product by methylation showed that the galactose residues were linked mainly through positions 1 and 3, but occasionally also through position 6 (7). In the present study, an attempt has been made to isolate a homogeneous polysaccharide from the mucilage, and to examine its structure by partial mercaptolysis.

In the first series of experiments, the milled alga was extracted with acetone, and then stirred for 2 hours with hot aqueous sodium acetate at pH 7. After three successive extractions of the residue in the same way, 73% of the dry weight of the alga had been removed as water-soluble products. Extraction in this manner appeared to be impeded by the presence of protein, of which the alga may contain 17–18% (N, 2.8%) (8). Furthermore, the extracts were contaminated with a brown pigment which could be removed only in part with decolorizing charcoal. In later experiments, when it was unnecessary to avoid slight degradation of the polysaccharides, both difficulties were overcome as described below.

A slurry of the alga in water, stirred at 75° C, was treated with dilute chlorous acid, added dropwise over a period of 30 minutes. During this time, the pH of the mixture fell slowly to 3.5. The pH was then brought immediately to 7 with sodium acetate, and extraction at 75° C was continued for 1 hour. In these cases, a single treatment caused dissolution of 88% of the alga, and the recovered polysaccharides were free from colored contaminants.

When potassium chloride (9, 10) was added to the aqueous extracts obtained by either method, a gelatinous precipitate was obtained of the potassium salt of a sulphated polysaccharide. This was collected and converted into the sodium salt by dialysis against aqueous sodium acetate. After three reprecipitations with potassium chloride in the same

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way, the purified product (sodium salt) had $[\alpha]_D +75^\circ \pm 2^\circ$ in water. It contained residues of galactose (43.1%), 3,6-anhydro-galactose (30.3%), and half-ester sulphate (as SO_3Na) (20.1%).

When a solution of the polysaccharide in 0.1 *M* sodium chloride was examined in the analytical ultracentrifuge, a single, sharp peak was observed. Chromatography of an acid-hydrolyzate of the material indicated the presence of galactose, a trace of xylose, and a component having an R_f similar to that of 5-hydroxymethyl-2-furaldehyde. Upon isolation, the galactose crystallized extensively; the crystals were of D-galactose.

Total mercaptolysis of the polysaccharide with ethyl mercaptan and concentrated hydrochloric acid gave a high yield of the crystalline diethyl mercaptals of D-galactose and 3,6-anhydro-D-galactose, in the molar ratio 1.3:1. These compounds were further characterized by conversion, respectively, into crystalline D-galactose, and into 3,6-anhydro-D-galactose phenylosazone.

Mercaptolysis for a shorter period of time afforded the above-named mercaptals (47%), together with a large amount (42%) of a disaccharide mercaptal (A). This component (A) was isolated by chromatography of the mixture on a column of coconut charcoal (11), followed by preparative paper chromatography. It crystallized, and was identical with an authentic specimen of 4-*O*-β-D-galactopyranosyl-3,6-anhydro-D-galactose diethyl mercaptal, as prepared by the partial mercaptolysis of κ-carrageenin (12). The identity of the two compounds was confirmed by comparison of their crystalline hexa-*O*-acetyl derivatives.

Demercaptallation of (A) with mercuric chloride and cadmium carbonate in water afforded a reducing disaccharide (B), from which a crystalline phenylosazone was prepared. Reduction of (B) with aqueous sodium borohydride yielded a crystalline glycitol (C), which formed a crystalline hepta-*O*-acetyl derivative (D). The physical constants of (C) and (D) agreed well with those recently reported by Clingman and Nunn (13) for 4-*O*-β-D-galactopyranosyl-3,6-anhydro-D-galactitol, and for its hepta-*O*-acetate, respectively.

These results suggest that a part of the mucilage of *Furcellaria fastigiata* is made up of a homogeneous polysaccharide which consists essentially of residues of D-galactose and 3,6-anhydro-D-galactose. The traces of xylose detected in hydrolyzates of the polysaccharide may have arisen from contaminating xylan. No evidence for the presence of monomer units derived from the L-series of sugars was obtained.

The high yield of the disaccharide mercaptal (A) indicates that the two types of sugar residue must be very evenly distributed throughout the macromolecule. As an idealized picture, the polysaccharide could be considered to consist entirely of repeating units represented by the disaccharide (B); the 30% molar excess of D-galactose residues might have arisen from a contaminating galactan which escaped detection in the ultracentrifuge. It is equally probable, however, that the polymer has a rather less highly ordered structure, with occasional small groups of contiguous D-galactose residues in the chains; a small proportion of the 3,6-anhydro-D-galactose residues may be similarly grouped.

As a result of the highly labile nature of 3,6-anhydro-galactosidic linkages, an investigation of the present type provides little information about them, beyond the fact that most of them must be directed towards D-galactose residues in the polysaccharide. However, when these results are considered together with the methylation studies of Dillon, O'Colla, and co-workers (7), it appears probable that most of the 3,6-anhydro-D-galactose residues are linked to position 3 of D-galactose residues. The positive specific rotation of the polysaccharide suggests, moreover, that most of these linkages are in the α-configuration.

It would follow that the polysaccharide is similar to κ -carrageenin, although the sulphate content is somewhat lower. Another polysaccharide of this type was recently isolated from *Hypnea specifera* by Clingman and Nunn (13).

EXPERIMENTAL

Paper chromatography was carried out on Whatman No. 1 filter paper. For preparative work, large sheets (57×46 cm) of Whatman No. 3MM paper were used; in these cases, the solvent was supplied to the sheets through short strips (57×8 cm) of Whatman No. 1 paper, which were attached to the main sheets with staples. The irrigant was either (a) butan-1-ol-ethanol-water (3:1:1 v/v) or (b) butan-1-ol-pyridine-water (6:4:3 v/v). Reducing sugars were located on the chromatograms by spraying with *p*-anisidine hydrochloride in butan-1-ol (14). Sugar mercaptals were located by spraying with silver nitrate in acetone, followed by ethanolic sodium hydroxide (15). Chromatographic mobilities are calculated relative to the solvent front (R_f).

Optical rotations were measured at $21^\circ \pm 2^\circ$ C; unless otherwise stated, the solvent was water. Melting points were determined with a Kofler block. Solvents were evaporated under diminished pressure at 30–45° C. X-Ray powder photography was carried out using chromium radiation and a vanadium filter; the powdered samples were mounted in the camera on lead-free glass fibers, to which they were attached with silicone grease. For sedimentation, a 0.2% w/v solution of the polysaccharide in 0.1 M sodium chloride was used. The ultracentrifuge, a Spinco Model E instrument, was operated at 59,780 r.p.m.

Sulphate was determined gravimetrically, after complete hydrolysis of the polysaccharide with 0.5 N hydrochloric acid (20 hours at 95° C), by precipitation as barium sulphate. Galactose and 3,6-anhydro-galactose were estimated by a modification (16, 17) of a method (18) for the simultaneous estimation of glucose and fructose. In an independent method, 3,6-anhydro-galactose was estimated selectively by a modification (16, 17) of the resorcinol method (19) for fructose. The results agreed well, and the figures given are averages.

Preparation of the Polysaccharide

The alga was collected near Pictou, Nova Scotia, in November, 1958. It was dried in a current of air at 45° C for 3 hours, and ground in a Wiley mill to pass a 20-mesh sieve. The product was extracted exhaustively with hot acetone, dried at room temperature, and used as follows.

Method (a)

The alga (100 g: 10% w/w moisture) was stirred in water (3 l.) containing sodium acetate (15 g) at 80° C for 2 hours. The mixture was then centrifuged while hot. The residue was extracted twice more in the same way, and then subjected to a final extraction for 6 hours. The final residue, when isolated and dried, weighed 21 g. The combined centrifugates (ca. 12 l.) were dialyzed against aqueous sodium acetate (0.1% w/v) for 24 hours. The solution was heated at 80° C with decolorizing charcoal (100 g) for 1 hour, and then filtered through Celite in a heated, sintered-glass funnel. To the clear, pale brown filtrate was added potassium chloride (400 g) in water (2 l.); the solution was allowed to cool slowly to 4° C, while being vigorously stirred. The gelatinous precipitate was collected by centrifugation, and dispersed in aqueous sodium acetate (0.1% w/v; 5 l.). This mixture was dialyzed against aqueous sodium acetate until the gel had dissolved (60 hours). The solution was diluted to 10 l. with water, heated with charcoal, and filtered as before, and again treated with potassium chloride. The gel was collected and reprecipitated twice more in the same way. It was finally dispersed in water (3 l.) and

dialyzed against aqueous sodium acetate until it had redissolved. The solution was poured into ethanol saturated with sodium acetate (10 l.). The precipitate was collected, washed thoroughly with aqueous ethanol (80% v/v), followed by absolute ethanol, then by ether, and dried over silica gel in a vacuum desiccator. The yield of light brown, fibrous polysaccharide (F-1) was 15.0 g.

Method (b)

The alga (50 g; 10% w/w moisture) was stirred in water (2 l.) at 75° C for 10 minutes. A solution of chlorous acid was prepared by treating aqueous sodium chlorite (4% w/v) with an excess of Amberlite resin IR-120. This solution (150 ml) was added, uniformly and dropwise, to the above slurry over a period of 30 minutes. At 5-minute intervals, aliquot portions were withdrawn and cooled, and the pH was measured with a Beckman pH meter.

Time (minutes)	0	5	10	15	20	25	30
pH	7.2	6.7	6.3	5.7	5.0	4.3	3.5

The mixture was then neutralized with sodium acetate (30 g) and sodium carbonate (4 g), and stirring at 75° C was continued for 1 hour. Water (3 l.) was added, and the mixture was centrifuged at 40–50° C. The residue, when isolated and dried, weighed 5.4 g. The centrifugate was filtered through Celite at 80° C, and then treated with potassium chloride (200 g) in water (1 l.), and allowed to cool. The gelatinous precipitate was collected and purified as described in method (a), with the exception that no charcoal was used. The final yield of white, fibrous polysaccharide (Na salt) (F-2) was 10.5 g.

Preliminary Examination of the Polysaccharide (F-1)

The following analytical values were obtained: $[\alpha]_D +75^\circ \pm 2^\circ$ (c, 0.2); ash, 14.6%; sulphated ash, 15.0%; SO_3Na , 20.1%; galactose (as $\text{C}_6\text{H}_{10}\text{O}_5$), 43.1%; 3,6-anhydrogalactose (as $\text{C}_6\text{H}_8\text{O}_4$), 30.3%. In the ultracentrifuge, a single, sharp peak was obtained which showed only slight spreading of the boundary.

A portion (1 g) was hydrolyzed with *N* sulphuric acid at 100° C for 12 hours. The solution was neutralized with barium carbonate, filtered, deionized (resins), and concentrated to a syrup (350 mg). Chromatography of the hydrolyzate in solvent (a) or (b) indicated the presence of galactose, a trace of xylose, and a component similar to 5-hydroxymethyl-2-furaldehyde. Separation of the galactose on a large chromatogram gave a syrup (260 mg) which had $[\alpha]_D +78^\circ$ (c, 2.6). It crystallized from methanol, and after one recrystallization from the same solvent, the yield of pure crystals was 190 mg. They had m.p. 165–166° C, unchanged on admixture with pure α -D-galactose, and $[\alpha]_D +139^\circ$ (by extrapolation) $\rightarrow +79^\circ$ (24 hours) (c, 1.0).

Total Mercaptolysis of the Polysaccharide

The polysaccharide (F-2; 10 g) was stirred with concentrated hydrochloric acid (70 ml) at 0° C for 10 minutes. Ethyl mercaptan (25 ml) was added over a period of 1 hour. The mixture was then allowed to warm slowly to 10° C, and stirring at this temperature was continued. The flask was kept closed to minimize evaporation of ethyl mercaptan. After 24 hours, more ethyl mercaptan (25 ml) was added. After a total time of 96 hours, the mixture was cooled to 0° C, and ice-cold methanol (800 ml) was added. The resulting homogeneous solution was neutralized with lead carbonate, filtered, and the filtrate and washings were concentrated to a syrup. This was dissolved in absolute methanol (300 ml); the solution was cooled to 0° C, and the small deposit of inorganic salt was removed by filtration. The filtrate was concentrated to a syrup (11.5 g). Chromatography of this product in solvent (a), followed by the use of the silver nitrate spray reagent, indicated

an intense black spot, R_f 0.65, corresponding to galactose diethyl mercaptal, and a light brown spot, R_f 0.90, corresponding to 3,6-anhydro-galactose diethyl mercaptal. Also detected were small spots corresponding to xylose diethyl mercaptal (R_f 0.77), to ethyl 1-thio-galactopyranoside (R_f 0.50), to free galactose (R_f 0.15), and to traces of reducing oligosaccharides (R_f 0-0.05).

(i) *D-Galactose Diethyl Mercaptal*

The above mercaptolysate was dissolved in water (100 ml), and the solution was cooled to 0° C, whereupon it solidified to a crystalline mass. This was lixiviated with ice-cold water. The crystals were collected (yield, 3.5 g), and recrystallized twice from methanol-ether. The pure product had $[\alpha]_D -3.7^\circ \pm 0.5^\circ$ (c , 0.7), and m.p. 141-141.5° C, unchanged on admixture with synthetic D-galactose diethyl mercaptal. The crystals (1 g), mercuric chloride (5 g), and cadmium carbonate (10 g) were heated in water (100 ml) for 2 hours at 50° C. The mixture was cooled and filtered, and the filtrate was saturated with hydrogen sulphide. Precipitated material was removed, and the solution was then neutralized with Amberlite resin IR-45. It was concentrated to a syrup (0.5 g), which was dissolved in a minimum of hot methanol. On cooling, crystals separated, and after recrystallization from methanol, the compound had m.p. and mixed m.p. with α -D-galactose, 165.5-166.5° C, and $[\alpha]_D +142^\circ$ (by extrapolation) $\rightarrow +80^\circ$ (14 hours) (c , 1.1).

(ii) *3,6-Anhydro-D-galactose Diethyl Mercaptal*

After collection of the D-galactose diethyl mercaptal, the aqueous filtrate was diluted to 500 ml with water, and then shaken 10 times with ether (10 \times 200 ml) in a separatory funnel. The combined ether extracts (2 l.) were dried with Drierite, filtered, and concentrated to 200 ml. When ligroin (b.p. 35-60° C) (100 ml) was added, a flocculent mass of crystals separated; they were collected by filtration (yield, 2.4 g), and recrystallized twice from ether-ligroin. From the filtrate, a second crop (1.1 g) of crystals was obtained. The pure crystals had $[\alpha]_D -9.8^\circ \pm 0.5^\circ$ (c , 0.4), and m.p. 111.5-112.5° C, unchanged on admixture with a synthetic specimen (12) of 3,6-anhydro-D-galactose diethyl mercaptal. A mixture with 3,6-anhydro-L-galactose diethyl mercaptal (m.p. 110-111° C), prepared by the mercaptolysis of agar (20), had a melting range of 109-134° C.

A sample of the compound (100 mg) was heated in water (15 ml) with mercuric chloride (500 mg) and cadmium carbonate (1 g) at 50° C for 2 hours. The mixture was cooled and filtered, and the filtrate was extracted exhaustively with ether. It was then heated with phenylhydrazine (0.2 ml), sodium acetate (1 g), and acetic acid (1 ml) at 80° C for 2 hours. The flocculent yellow precipitate was collected and recrystallized from methanol. The product had m.p. 217° C, unchanged on admixture with 3,6-anhydro-D-galactose phenylosazone (12), and $[\alpha]_D +75^\circ$ (15 minutes) $\rightarrow +54^\circ$ (20 hours, constant) (c , 0.2 in methanol). For 3,6-anhydro-L-galactose phenylosazone, Araki and Hirase (21) report $[\alpha]_D -75^\circ$ (initial) $\rightarrow -53^\circ$ (24 hours) (in methanol-pyridine).

(iii) *Ethyl 1-Thio- α -D-galactopyranoside*

The aqueous solution remaining after the extraction of 3,6-anhydro-D-galactose diethyl mercaptal was concentrated to a syrup (3.2 g). Chromatography indicated the presence of three major constituents. The mixture was separated on large chromatograms, to yield D-galactose (0.5 g), D-galactose diethyl mercaptal (1.2 g), and the other component, having R_f 0.50 in solvent (a), (0.6 g). This last component was obtained as a syrup having $[\alpha]_D +280^\circ$ (c , 2.5). It crystallized slowly on standing, and after three recrystallizations from butan-1-ol, it had $[\alpha]_D +318^\circ \pm 2^\circ$ (c , 0.6), and m.p. 152-153.5° C. For ethyl 1-thio- α -D-galactopyranoside, Fried and Walz (22) report $[\alpha]_D +320^\circ$, and m.p. 153.5-154° C. Calculated for $C_8H_{16}O_5S$: S, 14.3%. Found: S, 12.7%. Demercaptallation in the usual

way afforded D-galactose, $[\alpha]_D +78^\circ$, characterized by conversion into its 1-methyl-1-phenylhydrazine, m.p. 189°C .

Partial Mercaptolysis of the Polysaccharide

The polysaccharide (F-1; 10 g) was stirred at 0°C with concentrated hydrochloric acid (70 ml) for 10 minutes. Ethyl mercaptan (30 ml) was then added, and stirring at 0°C was continued for 20 hours. The mixture was then stirred at 10°C for a further 24 hours. The mercaptolysate (10.5 g) was recovered as described above. It was dissolved in water (50 ml) and the solution was cooled to 0°C . Crystals (1.2 g) of D-galactose diethyl mercaptal separated, and were collected by filtration. The filtrate was diluted with water, and extracted by shaking with ether. From the extract, 3,6-anhydro-D-galactose diethyl mercaptal (1.8 g) was recovered. The remaining aqueous solution was then extracted exhaustively with ether in a liquid-liquid extractor for 3 days. From the extract, a further quantity of D-galactose diethyl mercaptal (0.8 g) was recovered. The aqueous layer was then concentrated to a syrup (6.0 g). On chromatograms developed in solvent (a), and sprayed with the silver nitrate reagent, the presence was shown of (i) a small, black spot, R_f 0.67, corresponding to galactose diethyl mercaptal; (ii) a very large, light brown spot having R_f 0.60; (iii) a dark brown spot, R_f 0.50, corresponding to ethyl 1-thio-galactopyranoside; (iv) three very small spots having R_f 0.42, 0.30, and 0.27 respectively; (v) a spot, R_f 0.15, corresponding to free galactose; and (vi) spots corresponding to traces of reducing oligosaccharides.

Isolation of 4-O- β -D-Galactopyranosyl-3,6-anhydro-D-galactose Diethyl Mercaptal (A)

Owing to overlapping of the spots, it was not possible to isolate the major component (A; R_f 0.60 in solvent a) of the mixture directly by paper chromatography. The mixture (6.0 g) was therefore adsorbed on a column (14×4 cm) of coconut charcoal (11). Elution with aqueous ethanol (5% v/v; 2 l.) displaced D-galactose (0.8 g). Aqueous ethanol (7.5% v/v) then displaced ethyl 1-thio-D-galactopyranoside (0.6 g in 8 l.), followed by D-galactose diethyl mercaptal (0.4 g in 10 l.). Elution with 20% v/v aqueous ethanol then displaced traces of reducing oligosaccharides, and the components with R_f 0.30 and 0.27 in solvent (a) (0.2 g in 5 l.). Finally, aqueous ethanol (50% v/v; 6 l.) eluted a mixture (3.8 g) containing ca. 90% of component (A). This last fraction was purified by preparative paper chromatography, to yield a viscous, colorless syrup having $[\alpha]_D +14^\circ$ (c, 2.0). It was indistinguishable on chromatograms developed in solvent (a) or (b) from an authentic specimen of 4-O- β -D-galactopyranosyl-3,6-anhydro-D-galactose diethyl mercaptal, which was prepared from κ -carrageenin, and characterized by the late Dr. A. N. O'Neill (12). After drying over phosphorus pentoxide, it crystallized from absolute ethanol-ether, and had m.p. $116\text{--}117^\circ\text{C}$, undepressed on admixture with the authentic specimen.

A portion (100 mg) was heated at 80°C with pyridine (15 ml) and acetic anhydride (10 ml) for 1 hour. Excess of these reagents was then removed by distillation *in vacuo*, and the residue was washed by decantation with water. The residue crystallized from ethanol-water, and after three recrystallizations from the same solvents, the product had $[\alpha]_D +12^\circ$ (c, 0.4 in chloroform), and m.p. $121.0\text{--}121.5^\circ\text{C}$, unaltered on addition of authentic 4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-2,5-di-O-acetyl-3,6-anhydro-D-galactose diethyl mercaptal (12). X-ray powder photographs of the two hexa-O-acetates were identical.

4-O- β -D-Galactopyranosyl-3,6-anhydro-D-galactose (B)

A portion (1 g) of the disaccharide mercaptal (A) was demercaptallated with mercuric

chloride and cadmium carbonate in water in the usual way. Excess of mercuric chloride was removed by extraction with ether. The syrupy product (B; 0.7 g) reduced Fehling's solution in the cold, and restored the color to Schiff's reagent. Calculated for $C_{11}H_{19}O_9(CHO)$: reducing equivalent weight, 162. Found (by iodometric titration): 155.

A part of the syrup (25 mg) was heated in water (5 ml) with phenylhydrazine (0.1 ml), sodium acetate (0.5 g), and acetic acid (0.5 ml) at 80° C for 2 hours. On cooling, yellow crystals separated; they were collected, and after recrystallization from ethanol-ether, the product had m.p. 211–213° C, and $[\alpha]_D + 110^\circ \pm 8^\circ$ (c, 0.4 in methanol).

4-O-β-D-Galactopyranosyl-3,6-anhydro-D-galactitol (C)

The remainder of the above syrup (B), dissolved in water (20 ml), was treated with sodium borohydride (1 g), and the solution was allowed to stand overnight at room temperature. It was then treated with excess of Amberlite resin IR-120, and filtered. The filtrate and washings were concentrated to dryness, and boric acid was then removed by the repeated distillation of added methanol. The final residue (C; 0.6 g) crystallized spontaneously on cooling, and after recrystallization from methanol-ether, it had m.p. 172.5–173.5° C, and $[\alpha]_D + 12.7^\circ \pm 1.0^\circ$ (c, 0.12). For 4-O-β-D-galactopyranosyl-3,6-anhydro-D-galactitol, Clingman and Nunn (13) report m.p. 173–174° C, and $[\alpha]_D + 15^\circ$. Calculated for $C_{12}H_{22}O_{10}$: C, 44.2%; H, 6.75%. Found: C, 44.64%; H, 6.80%.

A part of the product (C; 100 mg) was acetylated with pyridine and acetic anhydride in the same way as for (A). The product (D) crystallized from ethanol as strongly birefringent needles, having m.p. 145.5–146.0° C and $[\alpha]_D - 6.2^\circ \mp 1.0^\circ$ (c, 0.2 in chloroform). For 4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-1,2,5-tri-O-acetyl-3,6-anhydro-D-galactitol, Clingman and Nunn (13) report m.p. 144–145° C, and $[\alpha]_D - 7.6^\circ$ (in chloroform). Calculated for $C_{26}H_{36}O_{17}$: C, 50.3%; H, 5.8%; Ac, 48.5%. Found: C, 50.02%; H, 6.01%; Ac, 48.10%.

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CHEMISTRY OF THE TRIFLUOROMETHYL GROUP

PART I. COMPLEX FORMATION BY PHOSPHINES CONTAINING THE TRIFLUOROMETHYL GROUP^{1, 2}

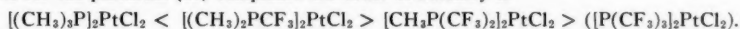
M. A. A. BEG AND H. C. CLARK

ABSTRACT

The formation of co-ordination compounds of $(\text{CH}_3)_3\text{P}$, $(\text{CH}_3)_2\text{PCF}_3$, $\text{CH}_3\text{P}(\text{CF}_3)_2$, and $\text{P}(\text{CF}_3)_3$, with boron trifluoride and platinum (II) chloride has been studied. The properties of the new compounds $(\text{CH}_3)_2\text{PCF}_3 \cdot \text{BF}_3$, $[(\text{CH}_3)_2\text{PCF}_3]_2\text{PtCl}_2$, $[\text{CH}_3\text{P}(\text{CF}_3)_2]_2\text{PtCl}_2$ are described, and it is hence concluded that the stabilities of the boron trifluoride compounds decrease in the order



while for the platinum (II) complexes the order of stability is



These two orders are related to the electronegativity of the trifluoromethyl group and its influence on the bonding properties of the phosphorus atoms.

INTRODUCTION

While a range of organometallic and organometalloidal trifluoromethyl compounds has been prepared, little quantitative information is so far available for the trifluoromethyl group. Since its electronegativity will differ widely from that of a normal alkyl or aryl group, these organometalloidal compounds may be expected to show unusual properties. A study has therefore been made of the effect of the trifluoromethyl group on the donor properties of substituted phosphines. Two types of addition products may be formed: (a) those containing only a σ -bond from phosphorus to the acceptor atom, as for example in $\text{F}_3\text{P} \cdot \text{BH}_3$, and (b) those in which both σ - and π -bonding occurs, usually between phosphorus and a transition metal, e.g. $(\text{R}_3\text{P})_2\text{PtCl}_2$. The effect of the electronegative trifluoromethyl group on the formation of σ - and π -bonds will vary and may be investigated by examining the properties of these two classes of compounds.

EXPERIMENTAL

Preparation of the Phosphines

Trimethylphosphine was prepared by the method of Mann and Wells (1). This reaction normally gives low yields, but it was found that, with strong cooling of the reaction vessel in an acetone-solid CO_2 mixture, yields of 60% could be regularly obtained. The phosphine was isolated as the silver iodide complex, which, when warmed *in vacuo*, readily evolved the phosphine.

The reaction of trimethylphosphine with trifluoroiodomethane, as described by Haszeldine and West (2), was used to prepare dimethyl trifluoromethylphosphine, but yields higher than 33% based on CF_3I could not be obtained. The reaction appeared to commence below -78° and was virtually complete after the mixture had stood at room temperature for about 30 minutes. Apart from the desired product and an involatile residue of tetramethylphosphonium iodide, a volatile white solid identified as dimethyl bis(trifluoromethyl)phosphonium iodide, m.p. 60° , was also found. The latter compound (0.472 g) reacted with excess aqueous sodium hydroxide at room temperature to give fluoroform (0.235 g) corresponding to the loss of two CF_3 groups. Purification of the

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dimethyl trifluoromethylphosphine was best achieved by thermal decomposition of its silver iodide complex as described by Haszeldine and West.

Methyl bis(trifluoromethyl)phosphine was prepared by reacting tris-trifluoromethylphosphine with methyl iodide as described by Haszeldine and West (3).

The preparation of tris(trifluoromethyl)phosphine from phosphorus and trifluoroiodomethane followed the methods of earlier workers (4).

Commercial boron trifluoride was used after purification by vacuum distillation. Platinum (II) chloride was prepared by heating chloroplatinic acid to 325° in an atmosphere of nitrogen. The complexes described below were prepared by reacting the phosphines with boron trifluoride or platinum (II) chloride in sealed, evacuated tubes. The identities of the boron trifluoride derivatives were determined from the ratios of the reactants and those of the platinum (II) chloride complexes by standard methods of analysis. Saturation pressures were measured with an isoteniscope, the boron trifluoride compounds being prepared directly in its bulb in order to avoid decomposition with moisture.

Compounds with Boron Trifluoride

(a) *Trimethylphosphine*.—The phosphine (0.1995 g, 2.60 mmoles) reacted immediately with boron trifluoride (0.1927 g, 2.79 mmoles) to give a white solid. The recovery of excess trifluoride (0.0031 g) gave a ratio phosphine:boron trifluoride of 1:1. The compound $(\text{CH}_3)_3\text{P} \cdot \text{BF}_3$ has been reported previously (5) but few of its properties have been described. It is decomposed slowly in moist air, and rapidly in water, acetone, and ethanol. It is only slightly soluble in chloroform and insoluble in carbon tetrachloride and carbon disulphide. The melting point is 126–130° (decomp.) and the saturation pressure is given by the equation $\log_{10} p \text{ (mm)} = 8.460 - (2627/T)$ in the range 25°–100°, whence the heat of sublimation is 11.98 kcal mole⁻¹.

(b) *Dimethyl trifluoromethylphosphine*.—The phosphine (0.2952 g, 2.27 mmole) reacted with boron trifluoride (0.1589 g, 2.27 mmole) to give a white solid which melted below room temperature to a viscous liquid. The compound showed the same behavior towards moist air and polar solvents as its trimethylphosphine analogue. The melting or freezing point could not be precisely determined since supercooling to a glass occurred. Softening of the glass took place at approximately -9° C. The vapor pressure of the compound is given by the equation $\log_{10} p \text{ (mm)} = 10.354 - (2146/T)$ whence the heat of vaporization is 9.68 kcal mole⁻¹.

(c) *Methyl bis(trifluoromethyl)phosphine*.—In this case, no reaction occurred after 120 hours at room temperature between the phosphine (0.2690 g) and boron trifluoride (0.0938 g). Cooling to -78° still allowed the boron trifluoride to be recovered and there was no sign of complex formation. Similarly, the treatment of tris(trifluoromethyl)phosphine (0.3106 g) with boron trifluoride (0.1934 g) failed to reveal the formation of any complex.

Compounds with Platinum (II) Chloride

(a) *Trimethylphosphine*.—The complex $[(\text{CH}_3)_3\text{P}]_2\text{PtCl}_2$ has been prepared previously (6) but it was here prepared for comparison with its trifluoromethyl analogues. Direct reaction between the phosphine and platinum (II) chloride in the absence of a solvent was very slow. In a benzene suspension, reaction was more rapid although the yield was still low. Thus trimethylphosphine (0.195 g) shaken for 24 hours with platinum (II) chloride (0.3345 g) in benzene gave only 0.10 g of the complex, a 20% yield. Higher yields could be obtained by using the method described by Jensen (7) for the preparation of the

corresponding triethylphosphine complex. This involved shaking an aqueous solution of potassium chloroplatinite (1.20 g) with the phosphine (0.43 g). The mixture was heated on a steam bath for 30 minutes, and the white complex was filtered, and washed with water, alcohol, and ether. Recrystallization from methanol gave a yield of 0.51 g, a 41% yield of bis(trimethylphosphine)dichloroplatinum (II). Found: Pt, 45.5; Cl, 17.0. Calc. for $[(CH_3)_3P]_2PtCl_2$: Pt, 44.7; Cl, 16.1%. The melting point is 324–326° and the dissociation pressure in the range 155–190° is given by the equation $\log_{10} p \text{ (mm)} = 6.510 - (2108/T)$, whence the heat of dissociation is 9.59 kcal mole⁻¹. The complex dissolves readily in chloroform, is sparingly soluble in ethanol, and almost insoluble in ether, benzene, and carbon tetrachloride. In water, particularly when heated, decomposition occurs and the free phosphine is evolved.

(b) *Dimethyl trifluoromethylphosphine*.—The reaction of the phosphine (0.412 g, 3.17 mmoles) with platinum (II) chloride (0.425 g, 1.59 mmoles) at room temperature for 48 hours in a sealed tube gave a pale yellow product, which was recrystallized from methanol to give white, needle-shaped crystals of bis(dimethyl (trifluoromethyl)-phosphine)dichloroplatinum (II). Found: Pt, 37.2; Cl, 13.2. Calc. for $[(CH_3)_2PCF_3]_2PtCl_2$: Pt, 37.1; Cl, 13.5%. The complex melted at 188–190° with decomposition and the dissociation pressure over the range 90–130° is given by the equation $\log_{10} p \text{ (mm)} = 7.969 - (2438/T)$ whence the heat of dissociation is 11.31 kcal mole⁻¹. It is soluble in alcohol, chloroform, and carbon disulphide and insoluble in ether, benzene, and carbon tetrachloride. It is not soluble in cold water, but reacts slowly with hot water to evolve fluoroform. Almost complete conversion (90%) to fluoroform is obtained on heating to 80° with 25% aqueous sodium hydroxide.

(c) *Methyl bis(trifluoromethyl)phosphine*.—This phosphine and platinum (II) chloride in a 2:1 ratio reacted only slowly and unreacted phosphine was always recovered from the reaction tubes. Extraction of the solid reaction product with carbon tetrachloride or methanol and evaporation of the extract gave yellow crystals of bis(methyl bis(trifluoromethyl)-phosphine)dichloroplatinum (II). Found: Pt, 29.9; Cl, 11.2. Calc. for $[CH_3P(CF_3)_2]_2PtCl_2$: Pt, 30.7; Cl, 11.2%. The melting point is 85–87° and the dissociation pressure in the range 80–140° may be expressed as $\log_{10} p \text{ (mm)} = 4.885 - (1258/T)$ whence the heat of dissociation is 5.76 kcal mole⁻¹. The complex is soluble in carbon tetrachloride, ether, acetone, and alcohol, but is insoluble in water. Hydrolysis (50% approx.) to fluoroform occurs with 25% aqueous sodium hydroxide at 80°.

(d) *Tris(trifluoromethyl)phosphine*.—The following experiments were performed in attempts to prepare a platinum (II) complex. In all cases the reactants were completely recovered and no sign of complex formation was observed. (i) Direct reaction of the phosphine (0.175 g) and platinum (II) chloride (0.132 g) at room temperature. (ii) The passage of the phosphine in a stream of nitrogen over platinum (II) chloride heated to 200°. (iii) Reaction of the phosphine and platinum (II) chloride in methanol. Several experiments were performed under this last set of conditions and in all cases the methanol acquired a yellow color and a few colorless crystals appeared to be formed. All attempts to isolate a product were unsuccessful, apparently because of decomposition.

Dipole Moments

Because of the low solubility of the platinum complexes and also their tendency, in certain cases, to decompose slowly in the presence of moisture, accurate dipole moments were not calculated. The dielectric constants were measured with a simple Ebach dielectric constant meter and dipole moments were calculated using Jensen's formula (8) for dilute solutions. The accuracy of the dipole moments is ± 0.5 D.

TABLE

Molar concentration	ϵ_{soln}	P_m	μ (D)
[(CH ₃) ₃ P] ₂ PtCl ₂ measured in chloroform:benzene (1:1) solution ($\epsilon_{\text{mix}} = 3.380$)			
0.000466	3.426	3320	
0.000977	3.441	3780	13.1 ± 0.5
[(CH ₃) ₂ PCF ₃] ₂ PtCl ₂ measured in chloroform solution ($\epsilon_{\text{CHCl}_3} = 4.947$)			
0.00985	4.982	1667	
0.00189	5.007	1806	9.2 ± 0.5
[CH ₃ P(CF ₃) ₂] ₂ PtCl ₂ measured in carbon tetrachloride solution ($\epsilon_{\text{CCl}_4} = 2.261$)			
0.00297	2.261		
0.00525	2.261		0

DISCUSSION

The addition compounds formed by phosphines with boron trifluoride result from dative σ -bond formation from phosphorus to boron. Smaller secondary effects such as back co-ordination may also be involved but these are of only minor importance. Evidence from other series of BF₃ derivatives (9), comparable to that described here, reveals that a decrease in the electron-donating power of the co-ordinating base produces a corresponding decrease in the stability of the molecular addition compound. As a qualitative measure of stability, we have here employed relative volatilities. The vapor pressure equations quoted above show the lower volatility and greater stability of (CH₃)₃P.BF₃ as compared with (CH₃)₂PCF₃.BF₃. The trifluoromethyl group thus markedly reduces the donor properties of the phosphorus atom. This is in accordance with a higher electronegativity and a smaller inductive effect for the trifluoromethyl in contrast to the methyl group.

Since the adduct (CF₃)₃P.BH₃ does not exist (10) and since borine adducts are generally more stable than their boron trifluoride analogues, it is not surprising that methyl bis(trifluoromethyl)phosphine- and tris(trifluoromethyl)phosphine-boron trifluoride adducts could not be isolated.

The possibility that steric interaction by the much larger CF₃ group is responsible for the observed decrease in stability must also be considered, although the extent of such interaction is difficult to determine accurately. The steric requirements will certainly be greatest for tris(trifluoromethyl)phosphine for which Bowen (11) has shown the CPC angles to be 100° and the CF₃ groups all to lie on the same side of the phosphorus atom. Also since there is some rearrangement of the planar BF₃ molecule towards a tetrahedral configuration on formation of the co-ordinate bond, it would appear that steric interaction between the CF₃ groups and F atoms must be comparatively small. For the other phosphines with fewer CF₃ groups, steric interactions will be of even less significance. The observed decrease in stability of the BF₃ adducts is therefore not due to steric effects.

The infrared spectra of (CH₃)₃P.BF₃ and (CH₃)₂PCF₃.BF₃ could not be completely resolved so that full interpretation is not possible. However, in both cases the B—F stretching frequencies at 1450 and 1505 cm⁻¹ in BF₃ were shifted to the 1175–1200 cm⁻¹. This is similar to the shifts observed for ketone-BF₃ complexes by Susz *et al.* (12). There is also a considerable shifting of bands in the 650–750 cm⁻¹ region. Since both the BF₃ bending and P—C (aliphatic) stretching frequencies occur in this region and since no other similar spectra are available for comparison, assignments have not been made.

In phosphine-platinum (II) co-ordination compounds, in addition to the formation of dative σ -bonds from phosphorus to platinum, strong $d\pi$ - $d\pi$ -bonding is also possible and appears to be of considerable importance in determining relative stabilities. As an extreme

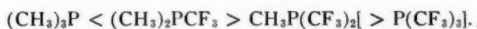
case, consider bis(trifluorophosphine)dichloroplatinum (II) $(F_3P)_2PtCl_2$ (13). Here the highly electronegative fluorine atoms reduce the electron donor properties of phosphorus, but at the same time cause considerable π -bonding which appears to involve the unshared d -electron pairs of platinum and the vacant $3d$ orbitals of the phosphorus atoms. The extent of this electron drift from platinum back to phosphorus is shown by the small dipole moment of 4.4 D. This indicates a *cis*-configuration and must be compared with values of 11–12 D for the *cis*-isomers of bis(trialkylphosphine)dichloroplatinum (II) complexes. Similarly, the substitution of trifluoromethyl for methyl groups may tend to give increased π -bonding between platinum and phosphorus although not to the same extent as phosphorus trifluoride.

The configurations of the complexes described earlier can be deduced from their colors, solubilities in polar and non-polar solvents, and their dipole moments. Bis(trimethylphosphine)dichloroplatinum (II) and bis(dimethyl trifluoromethylphosphine)dichloroplatinum (II) are obtained as the *cis*-isomers since they are white solids and have large dipole moments. Bis(methyl bis(trifluoromethyl)phosphine)dichloroplatinum (II) is isolated in the *trans*-form which is yellow-orange and has a zero dipole moment. It must be emphasized that these are the major components of reaction products prepared and recrystallized under the same conditions. In all three cases there were indications that the other isomer was also formed but only to the extent of less than about 5%. Since it is known that the isomer obtained under a given set of conditions may depend to some extent on relative solubilities, it would clearly be necessary to study in detail the *cis-trans* equilibria in order to determine unambiguously the relative stabilities of the isomers of the various complexes. However, since all our complexes could be prepared under identical conditions in the absence of solvents, the fact that different isomers are obtained with dimethyl trifluoromethylphosphine and methyl bis(trifluoromethyl)phosphine is significant and is discussed later.

The relative stabilities of these new phosphine complexes may be examined in several ways. Chemically, the trimethylphosphine complex appears the least stable since decomposition always occurs to a small extent during recrystallization from methanol, and to a much larger extent on reaction with warm water. Also, the solid compound always smells strongly of the free phosphine. In contrast the other two complexes were odorless solids which could be recrystallized without decomposition and which reacted only slowly with hot water. An accurate index of thermal stability is seen in the heats of dissociation calculated from the observed dissociation pressures, the values being 6.7 kcal mole⁻¹ for *cis*- $[(CH_3)_3P]_2PtCl_2$, 11.3 kcal mole⁻¹ for *cis*- $[(CH_3)_2PCF_3]_2PtCl_2$, and 5.8 kcal mole⁻¹ for *trans*- $[CH_3P(CF_3)_2]_2PtCl_2$. The process of dissociation probably involves the loss of a phosphine molecule and the formation of a dimeric bridged complex,



but it could alternatively result in the simultaneous loss of both phosphine molecules to give free platinum (II) chloride. Although the actual course of dissociation is unknown, the above values are considered a reasonable guide to relative stabilities of the platinum complexes and they show the order to be



Points of particular interest are: (a) the increase and then decrease in stability in the series as CF_3 is substituted for CH_3 ; (b) the non-existence, under the conditions so far studied, of a Pt(II) complex of tris(trifluoromethyl)phosphine; and (c) the fact that, under

the same conditions, dimethyl (trifluoromethyl)phosphine gives the *cis*-isomer, while methyl bis(trifluoromethyl)phosphine produces the *trans*-isomer. In platinum (II) complexes the greatest degree of π -bonding is obtained when the two π -bonding ligands are *cis* to one another (14). Substitution of the first methyl group by the more electronegative CF_3 group thus appears to give greater stability to the complex by causing a greater increase in π -bonding than is offset by the reduction in strength of the σ -bond. This can also be seen by a comparison of the dipole moment of 13.1 D for $[(\text{CH}_3)_3\text{P}]_2\text{PtCl}_2$ with that of 9.2 D for $[(\text{CH}_3)_2\text{PCF}_3]_2\text{PtCl}_2$. For the complex of methyl bis(trifluoromethyl)phosphine there might be expected to occur one of only two possibilities: (a) introduction of the second CF_3 group on each phosphine might produce even greater stability; or (b) the reduction in strength of the σ -bond may more than offset any increase in π -bonding so as to give a less stable complex. In either case, one might expect that the *cis*-isomer would be obtained. The occurrence of the *trans*-isomer is therefore unexpected, and can satisfactorily be explained, together with the non-existence of a tris(trifluoromethyl)-phosphine complex, in terms of steric hindrance. When models are drawn using the usual values of atomic radii, it can be shown that 2 trimethyl (or indeed any alkyl)phosphine molecules can be placed *cis* to one another about a platinum atom, but not 2 tris(trifluoromethyl)phosphine molecules. The observed effects are certainly not just due to the decreased donor properties of the phosphines since the *cis*-isomer of bis(trifluorophosphine)-dichloroplatinum (II) is known and is more stable than its *trans*-isomer. The importance of steric effects for the trifluoromethylphosphines is also shown by the fact that nickel carbonyl derivatives have been obtained (15) in which no more than 2 of the carbon monoxide molecules can be replaced by tris(trifluoromethyl)phosphine. In contrast, the more electronegative and more weakly electron-donating but much smaller PF_3 molecule can occupy all four positions to give $\text{Ni}(\text{PF}_3)_4$ (16).

Although these stability orders for the boron trifluoride and platinum (II) chloride derivatives might well be investigated further by the determination of thermodynamic values, particularly the thermodynamic differences between *cis*- and *trans*-isomers, the present information does emphasize the high electronegativity of the trifluoromethyl group, as well as the importance of π -bonding in transition metal complexes.

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HYDROGEN BONDING IN DIASTEREOISOMERIC α - β AMINOALCOHOLS: A REINVESTIGATION OF THE EPHEDRINES BY N.M.R.¹

JAMES B. HYNE²

ABSTRACT

The results of an n.m.r. study of the diastereoisomeric ephedrine and ψ -ephedrine molecules in non-polar solvents are interpreted and discussed in terms of the relative stabilities of the intramolecularly hydrogen-bonded conformers.

INTRODUCTION

The presence of two different asymmetric centers in the ephedrine molecule accounts for the existence of four optically active forms of the molecule. Previous configurational analysis of the ephedrines (1, 2, 3) has established the configuration of the two centers in all four forms of ephedrine as summarized in Table I. Considerable chemical evidence has accumulated which suggests that there is preferred spatial distribution of the hydroxyl and amino functional groups in the ψ -ephedrines which differs from that in the ephedrines.

TABLE I
Configuration of the ephedrines

$\begin{array}{c} \text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}(\text{NHCH}_3)\text{CH}_3 \\ \uparrow \quad \quad \uparrow \\ \text{C}_O \quad \quad \text{C}_N \end{array}$			
(+)- ψ -ephedrine	$\text{C}_O(+)\text{C}_N(+)$	(-)-ephedrine	$\text{C}_O(-)\text{C}_N(+)$
(-)- ψ -ephedrine	$\text{C}_O(-)\text{C}_N(-)$	(+)-ephedrine	$\text{C}_O(+)\text{C}_N(-)$

¹ C_O , center configuration related to (+)- and (-)-mandelamide.
² C_N , center configuration related to (+)- and (-)-alanine.

Emde (1) first suggested that this conformational difference existed and the work of Welsh (4), Nagai and Kanoa (5), and Fodor and Koczka (6) further suggested that in the ψ -ephedrines the hydroxyl and amino functional groups were spatially in a preferred gauche conformation, while in the ephedrines the *trans* disposition about the $\text{C}_O\text{—C}_N$ bond was preferred. Close (7) explained the production of an oxazolidone from ψ -ephedrine on fusion with urea compared with an imidazolidone on similar treatment of ephedrine on the basis of a preferred gauche disposition of the hydroxyl and amino groups in ψ -ephedrine compared with *trans* in ephedrine. This conformational difference is reflected in the mechanism of ring closure to form the oxazolidone or imidazolidone, in the former case by elimination of ammonia and in the latter case of water. Everett and Hyne (8) reported approximate calculations of the energetically most favorable conformations for the two forms of ephedrine based on the repulsive interactions between non-bonded groups on the C_O and C_N centers and ignoring specific interactions between the hydroxyl and amino groups. These rough calculations give surprisingly good agreement with the chemical evidence showing that in the ψ -ephedrine the angle between the $\text{C}_O\text{—OH}$ and $\text{C}_N\text{—NHCH}_3$ bonds, looking down the $\text{C}_O\text{—C}_N$ axis, is 60° and in the ephedrine case 180° .

Phillips (9) has reported the X-ray crystallographic data on both ephedrine and ψ -ephedrine hydrochlorides. In these crystal lattices the hydroxyl and amino functional

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groups were found to be *gauche* to one another in both forms of the hydrochloride. However, as Phillips points out, the presence of the chloride ion in the lattice probably constrains these groups to adopt a *gauche* conformation, but this need not apply under other conditions of aggregation of the ephedrine molecules. Kanzawa (10) has recently reported that the infrared spectra of (-)-ephedrine and (+)- ψ -ephedrine indicate a greater predominance of intramolecularly hydrogen-bonded species in solutions of the ψ -isomer in non-polar solvents, and interprets this observation in terms of the preferred *gauche* conformation of the hydroxyl and amino groups.

The development of high resolution n.m.r. techniques provides a further tool for the investigation of this type of problem, and although in the case of the ephedrines the conformational differences have already been convincingly demonstrated by other methods a reinvestigation by n.m.r. serves to establish the applicability of this technique to such problems. Various n.m.r. studies of the chemical shift associated with hydroxylic hydrogens have shown that the chemical shift depends upon the degree to which these hydrogens are involved in hydrogen bonding (11, 12, 13, 14). None of the previous n.m.r. studies of this kind, however, have considered the case where intramolecular hydrogen bonding is only possible in a particular conformer and the various conformers are separated by relatively low energy barriers resulting from steric hindrance to free rotation about a single bond. Clearly, the application of n.m.r. techniques to such problems would be of particular value in the many conformational problems associated with the stereochemistry of aminoalcohols, diols, and related systems. An additional advantage of the n.m.r. method over the infrared method lies in the fact that the n.m.r. technique involves measurement of the peak *position* which can be determined with considerably greater precision than the *areas* of infrared absorption peaks, which frequently overlap to a considerable extent.

If the conformational difference suggested by previous work is real then the ψ -ephedrine isomer should show a much higher degree of intramolecular hydrogen bonding which should be less sensitive to breakdown as a result of dilution compared with the ephedrine diastereoisomer in which there is a greater degree of intermolecular hydrogen bonding. A study of the chemical shift associated with the hydroxyl and amino hydrogens as a function of concentration should, therefore, reveal a difference in behavior in the two ephedrine forms. Furthermore, the intermolecular hydrogen bond might be expected to be more sensitive to temperature changes than the intramolecular bond. The results of the study of both the concentration and temperature dependence of the resonance frequency of the hydroxyl and amino hydrogens are reported in this paper.

N.M.R. SPECTRA

Spectra were measured with a Varian V 4300 spectrometer operated at a fixed frequency of 40 megacycles. Samples were spun in 12-mm inside diameter tubes and temperature maintained at $20^{\circ} \pm 1^{\circ}$ except where otherwise specified. Chemical shifts, in c.p.s. from benzene as an external standard, were measured by standard side-band techniques with an accuracy of ± 2 c.p.s. or better. Solutions were prepared by dilution of a master solution prepared by weight. Attempts to measure spectra in carbon tetrachloride as solvent were unsuccessful due to reaction of the ephedrines with the solvent and precipitation of hydrochlorides. A similar reaction was found to take place in chloroform but only after several weeks of standing and could not be detected when the solution was stored in the dark. Even under conditions of normal illumination no evidence could be found of reaction of this type during the normal period required to prepare solutions and take spectra.

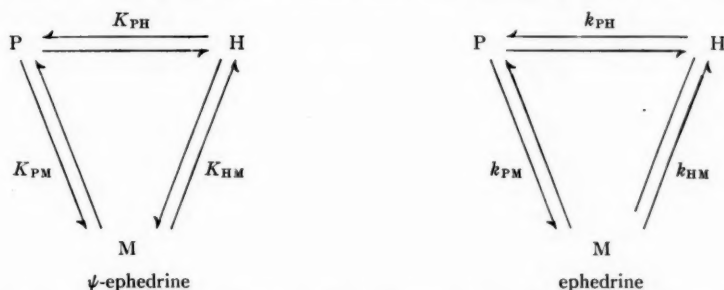
A single peak only was observed for both the NH and OH hydrogens (ν_{obs}) at all except very low concentrations at which it was difficult to distinguish between real splitting and noise effects. The single peak probably arises from rapid exchange of the hydrogens catalyzed by trace amounts of acid in the solvent.

Concentration Dependence of ν_{obs}

Figure 1 shows the dependence of the chemical shift associated with the NH and OH hydrogens on the concentration, c , in chloroform expressed in moles per liter of solvent. The observed difference in behavior for the two diastereoisomeric forms can be summarized as: (a) at any given concentration the frequency observed (ν_{obs}) for ψ -ephedrine is always lower than that for ephedrine; (b) the rate of increase of ν_{obs} with dilution is initially greater in the ψ -ephedrine case; (c) the ν_{obs} for ψ -ephedrine appears to approach a limiting value at the lowest concentrations measured, but that for ephedrine shows no such behavior within the experimental range of concentrations studied.

Huggins, Pimentel, and Shoolery (12) have previously reported chemical shift behavior of a similar type in the n.m.r. spectra of *o*-, *m*-, and *p*-chlorophenol. The concentration dependence of the *o*-chlorophenol OH resonance frequency reaches a maximum value for the frequency at low concentrations, while that of the *m*- and *p*-chlorophenol continues to increase throughout the dilution range studied. These authors attribute the differing behavior to the ability of the *o*-chlorophenol to hydrogen-bond intramolecularly, a phenomenon which is prohibited in the *m*- and *p*-chlorophenols for steric reasons.

In the ephedrine systems we consider a cyclic equilibrium between three species: P, an intermolecularly hydrogen-bonded polymer characterized by an NH/OH frequency ν_P ; H, an intramolecularly hydrogen-bonded monomer with frequency ν_H ; and M, an unhydrogen-bonded monomer with frequency ν_M . Clearly, we could consider various types of polymer, but as was shown previously by Saunders and Hyne (14) a model of this type involving equilibria between various types of *n*-mers leads to a result which is experimentally indistinguishable from one assuming a monomer-dimer equilibrium only. Assuming that the frequencies associated with the various species P, H, and M are



approximately equal for both forms (i.e. $\nu_P(\psi\text{-ephedrine}) = \nu_P(\text{ephedrine})$ etc.) a knowledge of the values of these frequencies would enable a quantitative interpretation of the observed data in terms of the equilibria postulated. Unfortunately, however, these values are not available from the data since the limiting value of ν_{obs} in either case can not be assumed to be the value for any single species of monomer. Despite the lack of this precise information we can interpret the data qualitatively in terms of the relative values of the equilibrium constants for the various processes in the cyclic equilibrium.

From the data in Fig. 1 we can deduce the relative magnitudes of ν_P , ν_H , and ν_M . It is known that the frequency associated with hydrogen-bonded hydrogen is lower than that

for unhydrogen-bonded hydrogen, therefore ν_P and ν_H must be less than ν_M . The relative values of ν_P and ν_H can be estimated from the observed slopes of the frequency versus concentration curves and the low concentration behavior. If ν_P and ν_H were equal, dissociation to hydrogen-bonded monomer H would not affect ν_{obs} and the observed greater slope of the ψ -ephedrine curve would be due entirely to easier dissociation to unhydrogen-bonded monomer M compared to the ephedrine case. This easier dissociation to unhydrogen-bonded monomer in the ψ -ephedrine system, however, is not in keeping with the observed behavior at low concentration. The approach to a limiting ν_{obs} which is considerably less than that observed for ephedrine clearly indicates that ψ -ephedrine does not dissociate more readily to the highest frequency monomer M. We therefore conclude that the relative order of magnitude of the frequencies must be $\nu_P < \nu_H < \nu_M$.

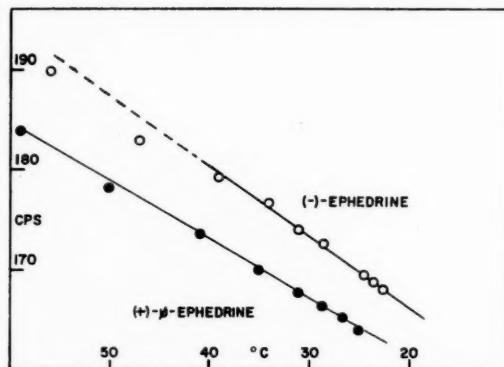


FIG. 1. The concentration dependence of resonance frequency for NH/OH hydrogens in c.p.s. from benzene (external) for ephedrine and ψ -ephedrine in chloroform solution. Concentration, c , in moles/liter.

The polymeric forms P of both ephedrines may dissociate to either one of two species, H or M. The data show that on initial dilution the ψ -ephedrine polymer dissociates more easily to the hydrogen-bonded monomer H with intermediate ν_H value. This will account for the greater observed slope and also the fact that at low concentrations the ν_{obs} tends to a limiting value which must be intermediate between that for ν_H and ν_M since both forms of the monomer exist in equilibrium. In terms of the dissociation constants this means that $K_{PH} > k_{PH}$ and $k_{PM} > K_{PM}$. That is, the hydrogen-bonded monomer of ψ -ephedrine is more stable relative to the unhydrogen-bonded monomer than the ephedrine counterpart, or $K_{HM} < k_{HM}$.

The concentration dependence of the NH/OH chemical shift for the two ephedrines therefore provides convincing evidence of the greater stability of the intramolecularly hydrogen-bonded ψ -ephedrine species, a conclusion which can only be rationalized in terms of the preferred gauche conformation of the hydroxyl and amino groups in the ψ -ephedrine diastereoisomer.

The Temperature Dependence of ν_{obs}

If, as has been suggested above, the ψ -ephedrine hydrogen-bonded species in the equilibrium mixture contain a greater proportion of intramolecularly hydrogen-bonded monomer than the ephedrine system at the same concentration, then the temperature dependence of ν_{obs} should differ in the two forms. This will only be true if the strengths of the inter- and intra-molecular bonds are different, but it seems reasonable to assume

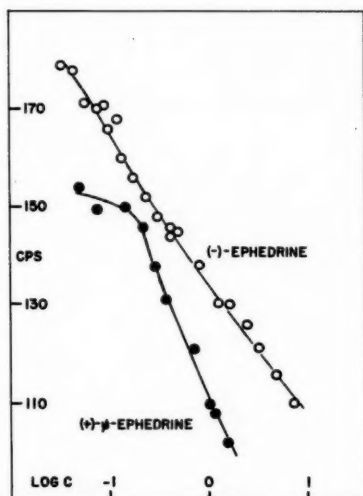


FIG. 2. The temperature dependence of resonance frequency for NH/OH hydrogens in c.p.s. from benzene (internal) for ephedrine and ψ -ephedrine in benzene solution.

that the intramolecular hydrogen bond will be less sensitive to temperature change than the intermolecular hydrogen bond. Figure 2 shows the temperature dependence of ν_{obs} for the two diastereoisomers in benzene solution. Benzene was used as a solvent rather than chloroform to avoid complication at higher temperatures arising from the reaction with solvent mentioned previously and in order to obtain a higher boiling solvent. Any shifts due to the anisotropy of the benzene will not seriously affect an argument based on the comparison of two isomers in the same solvent. The observed difference in temperature dependence is small but there is evidence at lower temperatures of a somewhat greater sensitivity to temperature in the case of ephedrine. Since only a proportion of the ψ -ephedrine hydrogen-bonded species will be intramolecularly hydrogen bonded and only these species will contribute to the reduction in temperature dependence compared with ephedrine the small observed difference is explicable. Furthermore, the intra- and intermolecular hydrogen bond strengths may differ by less than a kilocalorie and at most by no more than three or four. Although, in itself, the temperature dependence cannot be considered strong evidence for the preferred gauche conformation of the functional groups in ψ -ephedrine the small difference noted is in the direction to be expected on the basis of other evidence.

CONCLUSIONS

The concentration dependence of the chemical shift associated with the amino and hydroxyl hydrogens in the diastereoisomeric ephedrines provides good evidence for preferential residence of the ψ -ephedrine in the gauche form compared with the ephedrine isomer. Although the temperature dependence of the shift does not provide convincing evidence, the small effect noted does support the same conclusion. The work of Huggins, Pimentel, and Shoolery (12) on the chlorophenols has established the value of n.m.r. studies of intramolecular hydrogen-bonding phenomena where the hydrogen-bonded groups are not free to rotate by virtue of the order of the bond joining them. This work shows that

the method can be extended to systems where the restriction arises from steric factors rather than bond order. Therefore, studies of the dilution effect on chemical shift can provide additional criteria for establishing preferred conformations arising out of rotation about a single bond where the degree and type of hydrogen bonding vary with the conformation.

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THE STRUCTURE OF 2-*p*-DIMETHYLAMINOBENZYLIDENEINDOXYL AND ITS SALTS¹

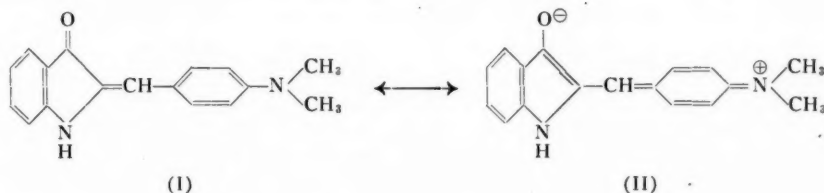
R. A. ABRAMOVITCH² AND A. M. MARKO³

ABSTRACT

2-*p*-Dimethylaminobenzylideneindoxyl has been shown to have mainly the dipolar quinonoid structure (II), though quaternization takes place at the dimethylamino nitrogen atom in the unperturbed structure (I). This has been established by a study of its infrared and ultraviolet absorption spectra and by a comparison of these with those of its monohydrochloride, its methiodide, and of 2-benzylideneindoxyl.

A quantitative method of analysis of indican in urine has been devised (1) which involves the reaction of the indican-containing solution with *p*-dimethylaminobenzaldehyde and spectrophotometric measurement of the red color developed. The color was shown to be due to 2-*p*-dimethylaminobenzylideneindoxyl (I), which could be isolated as a purple crystalline solid exhibiting dichroism, and which was identical with the product prepared by Noeling (2) from indoxyl-2-carboxylic acid and *p*-dimethylaminobenzaldehyde. This compound is reported (2) to be a dyestuff and the deep color of the crystals was noteworthy. The ultraviolet absorption spectrum in 95% ethanol exhibited an intense band at 510 mμ ($\epsilon = 21,300$) which did not seem to be compatible with the unperturbed structure (I). In dilute hydrochloric acid the color of the solution is a light orange-yellow, the intense band in the ultraviolet at 510 mμ being replaced by a weaker one at 497 mμ ($\epsilon = 15,620$).

The deep color of 2-*p*-dimethylaminobenzylideneindoxyl would be understandable if canonical structure (II) was the main contributor to the resonance hybrid:



Support of this suggestion was readily obtained from a consideration of the infrared and ultraviolet spectra of the base and some of its derivatives. In fact, the infrared spectrum of the solid dyestuff showed a medium-to-weak band at 1655 cm⁻¹. Because of the low intensity ($\Delta\nu_3$ for most of the bands in this region mentioned here are nearly comparable) and the position of this band, the band was considered unlikely to be due to the carbonyl group in (I). In fact, the ketonic carbonyl group in N-acetylindoxyl gives rise to a strong band at 1716 cm⁻¹ and that in 1-methylindoxyl to a band near 1750 cm⁻¹ (3). For the purpose of comparison the spectrum of 2-benzylideneindoxyl was recorded, and exhibited a strong conjugated carbonyl band at 1680 cm⁻¹. On the other hand, Edwards, Clarke, and Douglas (4) and Habgood and Marion (5a) have assigned a medium intensity band at 1668–1682

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cm^{-1} to the grouping $\text{C}=\text{N}^{\oplus}$ (see also Witkop and Patrick (5b)); such a grouping (conjugated in this case) is present in structure (II). The other bands observed in the $6\text{-}\mu$ region may also be interpreted on the basis of structure (II): thus the strong bands at 1617 (sh) and 1607 cm^{-1} may be attributed to the conjugated $\text{C}=\text{C}$ bonds and the band at 1558

cm^{-1} (s) to the highly conjugated enolate anion $\left(\text{C}=\text{C}^{\ominus}\right)$ (the enolate anion grouping is reported to give rise to a strong band at 1604 cm^{-1} (6)). Braunholtz, Ebsworth, Mann,

and Sheppard (7) have shown that compounds containing an NMe or an $\text{N}^{\oplus}(\text{Me})_2$ grouping exhibit a strong-to-medium band between 2760 and 2820 cm^{-1} . Salt formation or quaternization causes the disappearance of this band. No such band was observed in the infrared spectrum (KBr disk or hexachlorobutadiene mull) of 2-*p*-dimethylaminobenzylideneindoxyl. Evidence from ultraviolet absorption spectra also backs up the suggestion that (II) is the main contributory structure to the resonance hybrid. This evidence is as follows.

When a solution of 2-*p*-dimethylaminobenzylideneindoxyl in ethanol was treated with dilute hydrochloric acid, a marked change in color took place from reddish purple to yellowish orange. This was also accompanied by a change in the ultraviolet absorption spectrum (see Fig. 1). Thus, the intense band at 510 $m\mu$ underwent a hypsochromic shift

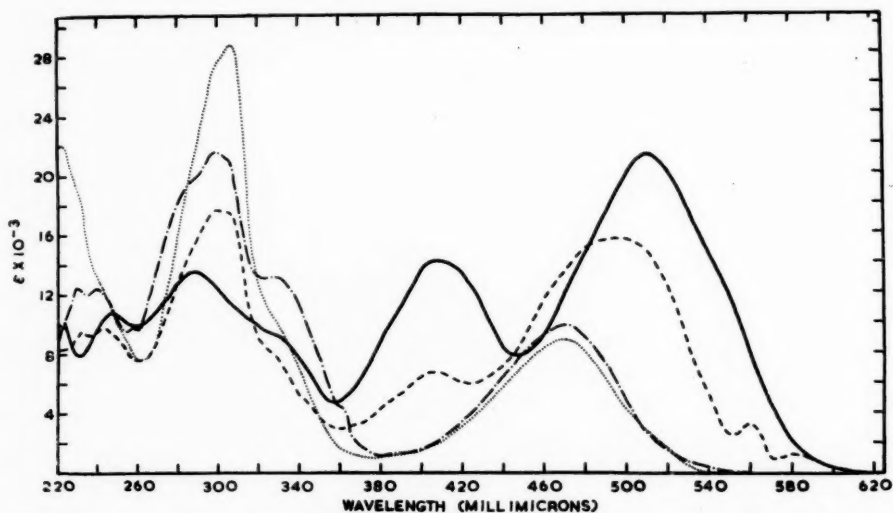
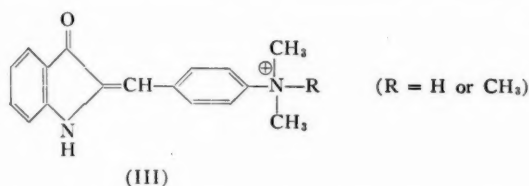


FIG. 1. — 2-*p*-Dimethylaminobenzylideneindoxyl in 95% ethanol. --- 2-*p*-Dimethylaminobenzylideneindoxyl in 95% ethanol containing a small amount of HCl. 2-Benzylideneindoxyl in 95% ethanol. 2-*p*-Dimethylaminobenzylideneindoxyl methiodide in 95% ethanol.

to 497 $m\mu$ as well as a decrease in intensity. The intensity of the 407- $m\mu$ band also decreased, whereas the 288- $m\mu$ band underwent a bathochromic shift to 300 $m\mu$ as well as an increase in intensity. Since the monohydrochloride could not be isolated in a pure state and it was felt to be important to determine which atom had been protonated

(the —O^\ominus in (II) or the $\text{—N(CH}_3)_2$ in (I)), the crystalline methiodide was prepared instead. This showed a similar ultraviolet absorption to that of the hydrochloride with the changes above even more intensified, i.e. a stronger hypsochromic shift and decrease in intensity in the longer wavelength band, and an increase in the intensity of the shorter wavelength band. It is possible that the hydrochloride is only partially formed in solution and exists in equilibrium with the free base, or that there exists a tautomeric equilibrium between the N and O protonated forms, both of which hypotheses could explain the smaller hypsochromic shift observed.* This would indicate that in the formation of the salt, attachment of the proton or of the methyl group took place preferentially at the dimethylamino group of (I), thus resulting in a decrease in color due to the loss of the quinonoid structure, and to the fact that no resonating structures similar to (I) \leftrightarrow (II) can be written for (III) without invoking an inadmissible pentavalent nitrogen atom.



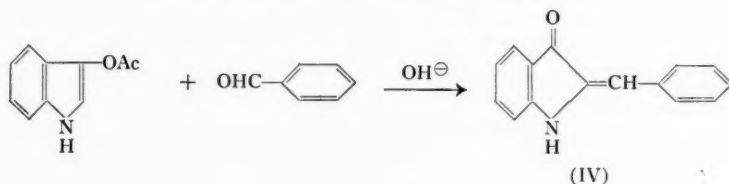
Support for structure (III; R = CH₃) was adduced from its infrared absorption spectrum which, unlike that of the parent 2-*p*-dimethylaminobenzylideneindoxyl, exhibited a strong band at 1686 cm^{-1} characteristic of the conjugated carbonyl group.

Conclusive supporting evidence for structures (II) (predominantly) and (III) assigned to the free base and salts respectively was obtained by a comparison of their ultraviolet absorption spectra with that of 2-benzylideneindoxyl (IV). Similar comparisons have very recently been carried out between *p*-dimethylaminoazobenzene and its methiodide, and azobenzene (9). Here the mesomeric effect of the dimethylamino group upon the ultraviolet absorption spectrum of the unsubstituted azobenzene is virtually nullified by quaternization, with the result that the spectra of azobenzene and *p*-trimethylammonium-azobenzene iodide are almost superimposable, whereas that of *p*-dimethylaminoazobenzene shows the expected bathochromic shift and increase in intensity due to the +M effect of the $\text{—N(CH}_3)_2$ group. When the ultraviolet absorption spectra of 2-*p*-dimethylaminobenzylideneindoxyl, its monohydrochloride, and its methiodide in ethanol were compared with that of 2-benzylideneindoxyl a comparable result to that reported (9) in the azobenzene series was observed (see Fig. 1). It is, therefore, concluded that though the quinonoid structure (II) is the main contributor to the structure of 2-*p*-dimethylaminobenzylideneindoxyl, quaternization occurs preferentially at the dimethylamino nitrogen atom.

When formation of the second conjugate acid of (II) was effected by dissolving the base in concentrated hydrochloric acid, the ultraviolet absorption spectrum changed markedly; the bands at 407 and 510 $\text{m}\mu$ in the base, and at 407 and 497 $\text{m}\mu$ in the monohydrochloride, disappeared and were replaced by a band at 380 $\text{m}\mu$. This solution was unstable and the color soon faded.

2-Benzylideneindoxyl (IV) had previously been prepared by Baeyer by heating indoxyl acid with benzaldehyde at 120° (10). In the present work it was found more

* Yeh and Jaffé (8) have recently presented evidence that the formally related first conjugate acid of *p*-dimethylaminoazobenzene consists of a tautomeric mixture of the ammonium and azonium-quinoid forms.



convenient to obtain this compound by the condensation of indoxyl-*O*-acetate with benzaldehyde in aqueous alkali, the yield of product being nearly theoretical.

EXPERIMENTAL

The infrared spectra were measured in potassium bromide disks and in Nujol mulls using a Perkin-Elmer Model 21 double beam spectrometer with sodium chloride optics. Ultraviolet absorption spectra were determined using a Beckman DK 2 recording spectrophotometer.

2-p-Dimethylaminobenzylideneindoxyl

A filtered solution of crude indican (0.7 g) (from the oxidation of indole with potassium persulphate (11)) in water (150 ml) was treated with a 3% ethanolic solution of *p*-dimethylaminobenzaldehyde (75 ml), followed by 6 *N* hydrochloric acid (100 ml) whereupon the solution turned dark brown. After it was stirred for 1 hour the mixture was filtered and the purple solid (0.3 g) discarded (this may arise due to the presence of impurities in the crude indican). The filtrate was neutralized with 10% sodium hydroxide (25 ml) and saturated aqueous sodium acetate solution (200 ml), the precipitate (2.2 g) filtered, washed with water, and then with light petroleum. Unreacted *p*-dimethylaminobenzaldehyde was removed by washing with hot light petroleum (4×30 ml) and then once with hot ethyl acetate (20 ml). The last procedure resulted in the loss of some of the desired product. The product was recrystallized from benzene-cyclohexane giving long needles, m.p. 236–238°, which were green by reflected and red by transmitted light. Crystallization from alcohol gave purple needles. Noelting (2) reports m.p. 226°–227° for this compound while Gossner (12) reports 231–232°. Calc. for $C_{17}H_{16}ON_2$: C, 77.30; H, 6.11; N, 10.60. Found: C, 77.50; H, 6.08; N, 10.52. λ_{\max} 248, 288, 407, 510, λ_{inf} 324 m μ ; $\epsilon \times 10^{-3}$ 10.89, 13.61, 14.21, 21.30, 9.54 (in 95% ethanol). λ_{\max} 232, 244, 300, 407, 497, λ_{inf} 324 m μ ; $\epsilon \times 10^{-3}$ 9.48, 9.79, 17.70, 6.66, 15.62, 8.44 (in ethanolic hydrogen chloride).

Infrared spectrum (KBr disk) (main peaks only): 3240, 1655 (mw) ($C=N^{\oplus}$), 1617

(sh) (s), 1607 (s) (conjugated $C=C$), 1558 (s) ($C=C-O^{\ominus}$), 1545 (NH), 1526 cm^{-1} . Identical values were observed when the measurement was carried out on a Nujol mull.

Attempted Preparation of 2-p-Dimethylaminobenzylidene-N-acetylindoxyl

N-Acetylindoxyl (1.75 g) and *p*-dimethylaminobenzaldehyde (1.6 g) were boiled under reflux in 80% ethanol (25 ml) with 5 drops of concentrated hydrochloric acid for 5 hours. On cooling, the solution deposited crystals of 2-*p*-dimethylaminobenzylideneindoxyl, identical with those obtained above from indican. Working up the mother liquors only led to the isolation of intractable tars which, on chromatography on neutral alumina, could only be resolved into a number of tarry fractions which could not be induced to crystallize. When the reaction was carried out using piperidine as the catalyst instead of

hydrochloric acid, similar results were obtained. The use of absolute instead of aqueous ethanol did not result in the isolation of any 2-*p*-dimethylaminobenzylideneindoxyl nor of any identifiable product.

2-*p*-Dimethylaminobenzylideneindoxyl Methiodide

This was prepared by adding an excess of methyl iodide to a suspension of 2-*p*-dimethylaminobenzylideneindoxyl in 95% ethanol; the flask was stoppered, shaken occasionally for 3 hours and left overnight. The purple solid gradually went into solution and the methiodide separated overnight as golden platelets which were recrystallized from ethanol after being washed with acetone. The product had m.p. 217–218° (after darkening at 204–205°). Calc. for $C_{18}H_{19}ON_2I$: C, 53.21; H, 4.68. Found: C, 53.02; H, 4.76. λ_{\max} 306, 470, λ_{\min} 294, 326 m μ ; $\epsilon \times 10^{-3}$ 28.70, 8.90, 24.50, 10.91 (in 95% ethanol). Infrared spectrum (Nujol mull) (main peaks only): 3300, 1686 (s) (>C=O) 1622 (s) (C=C), 1605 (s) (aromatic), 1589 (s), 1575 cm $^{-1}$ (sh) (w).

2-Benzylideneindoxyl

Indoxyl-*O*-acetate (0.22 g) and benzaldehyde (0.135 g) in water (10 ml) containing 10 drops of 4 *N* sodium hydroxide were warmed on a water bath. A flocculent yellow precipitate began to separate immediately and the warm mixture was shaken until no more dark brown oil remained. The cooled product was extracted repeatedly with ether, the extract concentrated to a small volume, and cooled in a freezer at -17° . The crystals, which were obtained in nearly theoretical yield, were filtered and recrystallized at a low temperature from ether, yielding orange rods, m.p. 177–178°. Baeyer (10) reports m.p. 176° for this compound. λ_{\max} 231, 241, 299, 470, λ_{\min} 284, 326, 358 m μ ; $\epsilon \times 10^{-3}$ 12.50, 12.42, 21.60, 9.88, 19.10, 13.19, 4.60. Infrared spectrum (Nujol mull) (main peaks only): 3260, 1680 (s) (>C=O), 1625 (s) (C=C), 1604 (s), 1590 (s), 1560 cm $^{-1}$ (sh) (m).

2-*p*-Dimethylaminobenzylideneindoxyl may be prepared conveniently and in high yield by substituting *p*-dimethylaminobenzaldehyde for benzaldehyde in this procedure.

ACKNOWLEDGMENTS

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THE PREFERENTIAL TOSYLATION OF THE *ENDO*-5-HYDROXYL GROUP OF 1,4;3,6-DIANHYDRO-D-GLUCITOL¹

R. U. LEMIEUX AND A. G. MCINNES

ABSTRACT

Reaction of 1,4;3,6-dianhydro-D-glucitol (isosorbide) with an equimolar amount of tosyl chloride in pyridine gave a fourfold greater yield of the *endo*-5-tosylate (IV) than of the *exo*-2-tosylate (III). Compound III reacted about 1.4 times more rapidly with tosyl chloride than did IV. The structures of III and IV were established by infrared spectroscopy and by their reaction with sodium methoxide. The *exo*-tosyloxy group of the monoacetate of III resists replacement by iodide ion.

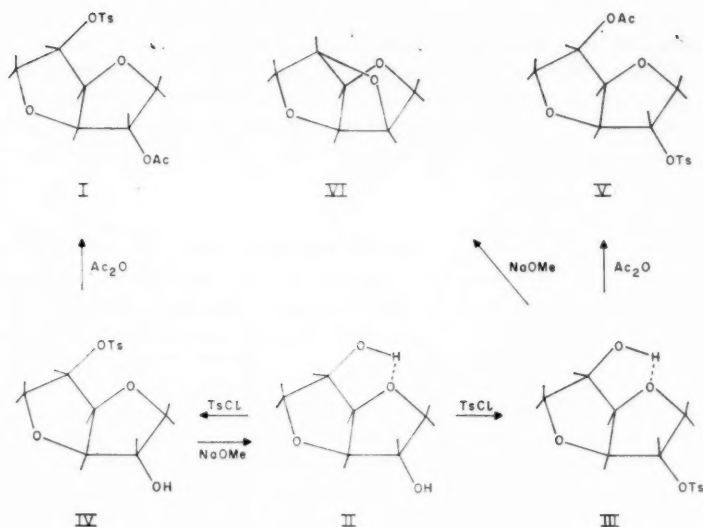
Cope and Shen (1) reported the preparation of a mono-*O*-tosyl mono-*O*-acetyl 1,4;3,6-dianhydro-D-glucitol (mono-*O*-tosyl mono-*O*-acetyl isosorbide). Since the compound was converted (1) to 1,4;2,5;3,6-trianhydro-D-mannitol (VI) on treatment with sodium *t*-butoxide, it was concluded that the tosyl group in I was situated at the *exo*-2-position (compound V). However, Cope and Shen (1) reported unequivocal evidence that a transtosylation reaction can take place under these conditions and, consequently, the monotosylate may have had the tosyl group at the *endo*-5-position as shown in structure I. Recently, Jackson and Hayward (2) have shown the compound to undergo replacement of the tosyloxy group when heated with sodium iodide dissolved in acetic anhydride. This observation was taken as proof that the tosyloxy group was at the *endo*-5-position. It is conceivable, however, that the *endo*-acetoxo group of 2-*O*-tosyl 5-*O*-acetyl isosorbide (V) can participate in the solvolysis of the tosyloxy group to lead to a 2,5-bridged acetoxonium ion, which could then react with iodide ion to give the iodoacetate isolated by Jackson and Hayward (2). Thus, the reaction of the compound with sodium iodide could not be taken as unequivocal evidence that it possesses the structure I.

A consideration of a molecular model for isosorbide (II) shows that the *endo*-5-hydroxyl group is eclipsed with the oxygen atom which bridges the 1- and 4-positions, whereas the *exo*-2-hydroxyl is eclipsed only with hydrogen atoms. The non-bonded interaction between the eclipsed oxygen atoms should be especially unfavorable since it brings into close opposition carbon-to-oxygen bonds polarized in the same direction. This contention is supported by the fact that D-glucitol is converted more readily to the 1,4-anhydride which possesses a 2,3-*trans*-glycol, then to the 3,6-anhydride which possesses a 4,5-*cis*-glycol (3). It could be anticipated that the *endo*-5-hydroxyl group of isosorbide would be intramolecularly hydrogen bonded to the eclipsing 4-oxygen atom. This conclusion was supported by the observation (see below) that the *endo*-5-hydroxyl group of 2-*O*-tosyl isosorbide (III) in fact is involved in an intramolecular hydrogen bond.

Therefore, one might expect (1) that the *exo*-2-hydroxyl group of isosorbide (II) would undergo tosylation substantially more rapidly than the sterically shielded and hydrogen-bonded *endo*-5-hydroxyl group. *The main purpose of this communication is to show that precisely the opposite is in fact the case.* This observation clearly has an important bearing on the general subject of preferential esterification of alcoholic hydroxyl groups in the field of carbohydrate chemistry and in particular on the hazards of introducing

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Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Ontario. This paper is to be a portion of a thesis to be submitted by A. G. McInnes for the Ph.D. degree.



notions on the subject derived from studies of simple alicyclic alcohols into the field of carbohydrate chemistry.

Isosorbide (II) was reacted with 1 mole equivalent of tosyl chloride in pyridine at 5° for 40 hours (1, 2). The ditosyl derivative was obtained in 17.1% yield. The syrupy residue was chromatographed on silicic acid with chloroform as developing phase to yield a crystalline monotosylate (III) in 11.7% yield and an isomer (IV), which has resisted crystallization, in 45.4% yield. Acetylation of IV yielded the monotosyl monoacetate (I) previously prepared by Cope and Shen (1). Acetylation of the crystalline monotosylate (III) led to a mono-*O*-tosyl mono-*O*-acetyl derivative of II which has not crystallized. The structures of the monotosylates III and IV were readily established through their behavior in presence of sodium methoxide. Compound III consumed the base about 40 times more rapidly than IV at room temperature and led to the formation of 1,4;2,5;3,6-trianhydro-*D*-mannitol (VI). On the other hand, IV when heated in the presence of sodium methoxide was converted to isosorbide (II) in excellent yield. Clearly, therefore, compounds III and IV have the structures shown. This conclusion was supported by the fact that the compounds III and IV showed absorption maxima for the hydroxyl groups, in the infrared, at 3564 and 3624 cm^{-1} , respectively, when 0.0025 *M* in carbon tetrachloride. These results indicate intramolecular hydrogen bonding in compound III which can only be possible with the hydroxyl group at the *endo*-5-position. The *O*-acetyl derivative of III (V) was recovered in high yield after treatment with sodium iodide in refluxing acetic anhydride for 2.5 hours. Consequently, the acetoxy group of V is in fact not well disposed for participation in the dissociation of the tosyloxy group. We have confirmed the observation (2) that I undergoes facile replacement of the tosyloxy group by iodine under these conditions. It is of interest that compound I resisted refluxing in 4:1 acetic acid - acetic anhydride containing potassium acetate for 24 hours.

The phenomenon of the preferential tosylation of the *endo*-hydroxyl group of I was

further substantiated by a study of the rates of tosylation of the monotosylates III and IV. The compound with the *endo*-hydroxyl group (III) reacted with tosyl chloride in pyridine at 25° approximately 1.4 times more rapidly than the isomer with the *exo*-hydroxyl group. It is not known whether or not this phenomenon is unique for the isosorbide structure. However, the literature suggests it may be of general importance in the esterification of polyhydric compounds. This matter is receiving further attention in this laboratory.

EXPERIMENTAL

Isosorbide (II) was prepared by the procedure of Montgomery and Wiggins (4). The white crystalline product melted at 62–63.5° (uncorr.) with $[\alpha]_D +44.6^\circ$ (*c*, 1.78 in water) and $+65^\circ$ (*c*, 2.94 in pyridine). The reported values are m.p. 61.9–64°, $[\alpha]_D +44.8^\circ$ (*c*, 2.22 in water) and $+64.9^\circ$ (*c*, 2.32 in pyridine) (5).

Reaction of Isosorbide (II) with Tosyl Chloride

Isosorbide, 13.2 g (0.905 mole), was dissolved in 100 ml pyridine and cooled to -5° . An equimolar amount of tosyl chloride (*p*-toluenesulphonyl chloride) was added and the reaction mixture stored at 5° for 46 hours. Any tosyl chloride present at the end of the reaction time was destroyed by the addition of 5 ml of distilled water to the reaction mixture, which was subsequently poured into 250 ml of distilled water and extracted with three 150-ml aliquots of chloroform. The combined chloroform extract was washed with concentrated hydrochloric acid to remove pyridine and then washed free of acid with distilled water. After drying over anhydrous sodium sulphate the chloroform solution was evaporated under reduced pressure at 50° to yield 22.6 g of a syrupy residue. The residue was dissolved in 100 ml 95% aqueous ethanol, and after the solution was left to stand overnight at 5°, 5.02 g of a white crystalline compound, m.p. 96–97° (uncorr.), was precipitated. The melting point and infrared spectrum of the substance were consistent with those expected for 2,5-di-*O*-tosyl isosorbide (6). The filtrate on evaporation under reduced pressure yielded 17.53 g of syrup.

The syrupy residue was chromatographed on 400 g silicic acid (Mallinckrodt) which had previously been activated at 120° for 24 hours. When the chromatogram was developed with chloroform, three fractions were cleanly separated in the following order: (a) a white crystalline compound, 2.00 g, the infrared spectrum of which was identical with that of 2,5-di-*O*-tosyl isosorbide; (b) a white crystalline compound (III), 3.18 g (11.7% of theory based on isosorbide), which after recrystallization from ethyl acetate melted at 108–109° with $[\alpha]_D +47.7^\circ$ (*c*, 1.86 in chloroform); and (c) a colorless syrup (IV), 12.31 g (45.4% of theory), $[\alpha]_D +57.9^\circ$ (*c*, 4.27 in chloroform). The total yield of ditosylate was 17.1% of theory.

A study, using a Beckman DK2 spectrometer, of the infrared spectra in the O—H stretching region of 0.0025 molar solutions of III and IV in carbon tetrachloride showed absorption at 3564 cm^{-1} and 3624 cm^{-1} , respectively. The latter is characteristic of the stretching vibration of a non-bonded secondary hydroxyl group, whereas the former shows a shift to lower frequency of 60 cm^{-1} which is characteristic of hydroxyl groups forming intramolecular hydrogen bonds.

Acetylation of 2-O-Tosyl (III) and 5-O-Tosyl Isosorbide (IV)

Samples of III, 1.74 g, and of IV, 5.31 g, were acetylated in pyridine with acetic anhydride at 5° to yield 1.80 g (90% theory) of 2-*O*-tosyl 5-*O*-acetyl isosorbide (V) and

5.70 g (94% theory) of 2-*O*-acetyl 5-*O*-tosyl isosorbide (I), respectively. V was a colorless oil, $[\alpha]_D +83.6^\circ$ (*c*, 3.43 in chloroform), whereas I crystallized from methanol, 5.0 g (83% theory), m.p. 65.5–66° (uncorr.), and $[\alpha]_D +79.2^\circ$ (*c*, 3.54 in chloroform). Reported (2) for 2-*O*-acetyl 5-*O*-tosyl isosorbide (I), m.p. 64–65° and $[\alpha]_D +77.9^\circ$ (in chloroform). The nuclear magnetic resonance spectra of compounds I and V were in agreement with those expected for mono-*O*-acetyl mono-*O*-tosyl derivatives of isosorbide; furthermore, the infrared spectra were very similar. There could therefore be no doubt as to the composition of I.

Reaction of (III) and (IV) with Sodium Methoxide

The compounds III, 0.345 g (1.15 mmoles), and IV, 0.2905 g (0.97 mmole), were dissolved in 10 ml of methanol approximately 0.2 *N* in sodium methoxide and left standing at room temperature. At intervals, over a period of 72 hours, 1-ml aliquots were taken and titrated with 0.064 *N* hydrochloric acid. At the end of the reaction period, III had consumed 0.108 milliequivalent (94% theory) and IV 0.065 milliequivalent (17% theory) of the sodium methoxide. Assuming second-order kinetics, the ratio of the rate constants, k_{III}/k_{IV} , was approximately 40.

Compounds III, 0.2005 g (0.667 mmole), and IV, 0.4585 g (1.53 mmoles), were refluxed with 2 ml and 4 ml, respectively, of methanol approximately 1 *N* in sodium methoxide for 8 hours. After cooling to room temperature, the excess sodium methoxide was neutralized with solid carbon dioxide. The reaction mixtures were taken to dryness at room temperature under reduced pressure and the residues extracted with ether and acetone, respectively. After solvent removal, the residues were distilled under reduced pressure. Compound III yielded 0.0689 g (81% theory) of a crystalline compound, m.p. 68–68.6° the infrared spectrum of which showed no absorption in the O—H stretching or aromatic skeletal vibration regions and was consistent with that expected for 1,4;2,5;3,6-trianhydro-*D*-mannitol (VI). The trianhydride (VI) was reported (1) to melt at 66.5–67.2°. On the other hand, IV yielded 0.1566 g (70% theory) of a crystalline compound whose infrared spectrum was identical with that of isosorbide (II).

Rates of Tosylation

The rates of tosylation of III and IV were compared by reacting 0.2256 g (0.75 mmole) of the compounds with 2 mmoles of tosyl chloride in 5 ml of pyridine at 25°. One-milliliter aliquots of the solutions were taken at intervals and added to 5 ml of 90% aqueous pyridine and left standing for 5 minutes. Ten milliliters of distilled water was then added and the free acid determined by titration with 0.0882 *N* sodium hydroxide using phenolphthalein as indicator. A solution containing only tosyl chloride in the same molar concentration was used as control. The reaction of III was complete after 28 hours, whereas IV had reacted to the extent of 72% of theory after this time. Assuming second-order kinetics the ratio of the rate constants for the two reactions, k'_{III}/k'_{IV} , was approximately 1.4.

Reaction of Sodium Iodide with I and V

The compounds V, 1.43 g (4.2 mmoles), and I, 3.43 g (10 mmoles), were refluxed with 20 ml and 50 ml, respectively, of a 0.5 *M* solution of sodium iodide in acetic anhydride. After 2.5 hours the solutions were cooled to room temperature and the sodium tosylate was recovered by filtration and weighed as described by Jackson and Hayward (2). Compound V yielded 0.060 g (7.4% theory) and I yielded 1.78 g (92% theory) of sodium *p*-toluenesulphonate.

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ADSORPTION EQUILIBRIA OF HYDROGEN, DEUTERIUM, AND THEIR MIXTURES. PART I¹

D. BASMADJIAN²

ABSTRACT

Adsorption isotherms of hydrogen and deuterium have been measured at temperatures of 75–90° K and pressures up to 760 mm Hg on the following six adsorbents: charcoal (2), silica gel, and Linde molecular sieves type 4A, 5A, and 13X.

Deuterium was found to be adsorbed to a greater extent than hydrogen in all cases investigated, its isosteric heat of adsorption exceeding that of hydrogen by 50 to 300 cal/mole.

Binary adsorption isotherms were determined on the same adsorbents in the range 10–90% D₂ at temperatures of 75 and 90° K and a total pressure π of 750 and 200 mm Hg. The analyses were performed by the thermal conductivity method using thermistor sensing elements in a static system at atmospheric pressure. The device proved of exceptional stability, requiring no recalibrations and yielding an analytical accuracy of better than 0.02% deuterium content. The binary separation factors α were found to be constant over the concentration range investigated, with values for α varying from about 1.25 on charcoal to 2.54 on type 4A molecular sieves at 75° K and 750 mm Hg. The results suggest that the variations in α are due mainly to differences in chemical composition of the adsorbents rather than pore size, surface area, or origin of the materials.

INTRODUCTION

Among isotopes of the same element or compound the heavier species are usually preferentially adsorbed. The effect becomes more pronounced with decreasing molecular weight and experiments in this field have therefore mostly dealt with low molecular weight substances such as the neon (1, 2) and hydrogen isotopes. Separation of the latter by means of sorption has been investigated by a number of workers (Table I).

TABLE I
Summary of literature data on deuterium enrichment by sorption

Adsorbent	Temp., ° K	Pressure, mm Hg	Separation factor*	Ref.
(1) Binary equilibria				
Silica gel	20	10 ⁻³	20–25	2
	78		4.5	
	90		3.0	
Silica gel	50–55	10 ⁻³	~20	3
Charcoal	65	10 ⁻³	~2–5	3
Charcoal	77	760	1.2	4
Alumina	20	?	~30	5
(2) Enrichment by desorption				
Charcoal	Liquid air	?	Pure fractions obtained	6.7
Charcoal	Liquid air	50–0	~1.15	8
Charcoal	65	~10 ⁻³	2–5	3
Silica gel	49–55	~10 ⁻³	4–40	3
Silica gel	78–90	10 ⁻⁴	7.8–5	2
Silica gel	20	10 ⁻⁴ –10 ⁻⁵	40±10	2
Silica gel	20	10 ⁻⁴ –10 ⁻⁵	"Up to 100"	9

*The separation factor is defined as the ratio of adsorbed phase to gas phase mole fractions, $\alpha = (X_{D_2}/X_{H_2})/(Y_{D_2}/Y_{H_2})$.

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Contribution from the Department of Applied Chemistry and Chemical Engineering, University of Toronto, Toronto, Ontario. Excerpts from thesis submitted in partial fulfillment of requirements for the degree of Doctor of Philosophy.

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The measurements usually consist in determining equilibrium separation factors (relative adsorptivities) α or analyzing the fractions obtained by slow desorption. A number of authors have also dealt with the gas chromatographic separation of the isotopes using supported palladium (10, 11) and type 5A Linde molecular sieves (12) as adsorbent.

From the results published so far, three major trends may be distinguished.

(a) Equilibrium separation factors show a marked increase with decreasing temperature and pressure, particularly at low values of the latter.

(b) By using the process of slow desorption, the equilibrium enrichment may be increased by factors as high as 1.7 (2).

The majority of data have been measured under conditions designed to yield maximum separations, i.e. pressures of 1 micron Hg or less and temperatures as low as 20° K. There are no published values of separation factors measured at temperatures and pressures suitable for use in the large-scale recovery of deuterium from natural hydrogen (75 to 100° K, 1 atm and above). The low values of α on charcoal at 77° K and 1 atm reported by Strange (4) give little reason to expect spectacular separations at these conditions and raise the problem of obtaining improved enrichments by means other than those mentioned above. The best prospects for achieving this appear to be in varying the adsorbent composition. Melkonian and Reps (2) have reported the enrichment on silica gel to be higher than on charcoal and it was thought to be of interest to measure separation factors on these and a number of other high capacity adsorbents at temperatures of liquid air and atmospheric pressure. In addition to charcoal and silica gel, measurements were made on the newly developed synthetic zeolites, Linde molecular sieves, which afford a means for determining any possible effects due to pore size. Single component isotherms of hydrogen and deuterium were also measured to provide additional data for the interpretation of the binary isotherms.

EXPERIMENTAL

The apparatus used is shown schematically in Fig. 1. Binary equilibria were determined by circulating hydrogen-deuterium mixtures of varying composition over the cooled adsorbent, equilibrium being assumed when the conductivity readings showed no further change (within $\pm 0.02\%$ D₂) over a period of $\frac{1}{2}$ hour. This was usually achieved within 2 to 3 hours after circulation was started. The adsorbed gases were then removed by means of the Toepler pump, and after the total volume was measured a sample was admitted to the conductivity cell for analysis. Single component isotherms were determined in the usual manner by admitting successive portions of the gases from a calibrated burette to the adsorbent. Pressures were measured by means of a McLeod gauge (below 5 mm Hg) and a U-tube manometer read to 0.05 mm Hg with a kathetometer. Constant readings were usually obtained within $\frac{1}{2}$ hour after the gases were admitted.

Liquid oxygen served as thermostat liquid, the appropriate temperature ($\pm 0.05^\circ$) being maintained by pumping down the charge by means of aspirators through manually operated control valves. Temperatures were measured with calibrated oxygen and nitrogen manometers.

The binary gas mixtures were circulated by means of an oscillating mercury column contained in a side-arm between two ground-in glass valves. The reciprocating motion was generated by the alternating action of a vacuum pump and a solenoid relief valve.

Analytical Procedure

Analysis of the deuterium-hydrogen mixtures was carried out by the thermal conductivity method (13). Figure 2 shows a schematic diagram of the analysis cell and

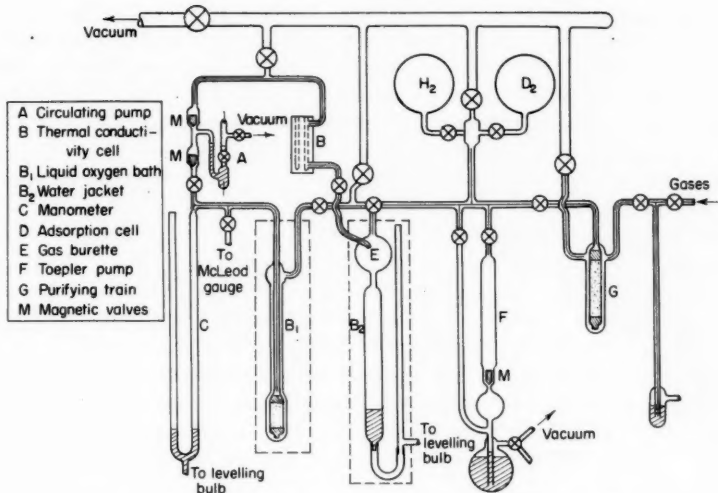


FIG. 1. Apparatus for the measurement of adsorption equilibria.

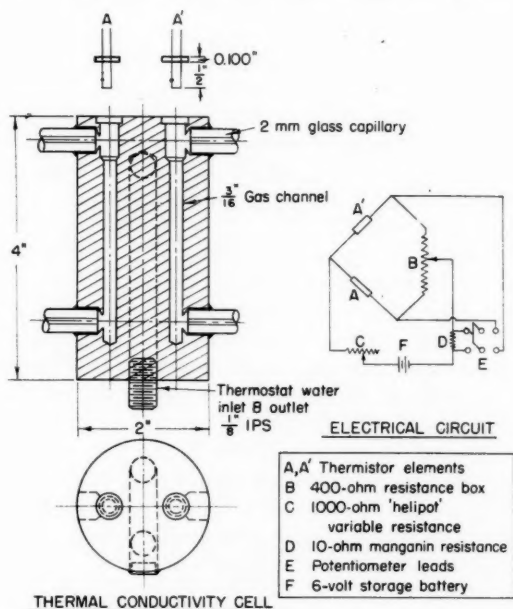


FIG. 2. Apparatus for the analysis of deuterium-hydrogen mixtures.

Wheatstone bridge circuit. Considerable difficulty was experienced in eliminating the drift caused by the instability of the sensing elements and ambient temperature fluctuations. Platinum or tungsten wires used by previous workers (2, 6, 13-17) proved unsatisfactory as they required constant recalibration or elaborate precautions which resulted only in partial elimination of the drift (16). The danger, in addition, of a possible

reaction of the isotopes to HD in contact with the hot filaments led to the adoption of thermistors as sensing elements. These units, consisting of tiny, glass-coated beads of semiconducting oxides, could be completely stabilized by annealing at 100° C for a period of 3 weeks. The small size and low operating temperature of the elements makes it unnecessary to analyze at accurate reduced pressures, in order to minimize convection currents, as suggested by Trenner and others (14, 16). The bridge was balanced with both sides of the cell containing pure hydrogen at 1 atm and the current input set at approximately 5 ma. A Leeds Northrup type K-2 precision potentiometer was used to measure bridge unbalance, which varied almost linearly with deuterium content of the sample, ranging up to a maximum of 150 mv for pure deuterium. Current input was controlled within 10^{-6} amp by adjusting the potential drop measured across a standard resistance, and the cell was kept at constant temperature by pumping water thermostated to 1/50° C through the cell body. The analytical accuracy attained in this manner was better than $\pm 0.02\%$ deuterium content, the readings being reproducible over a period of several months. The performance exceeds that of previous units described in the literature and could quite possibly be improved even further if the device is used in a flow system (11, 12) where convection and ambient temperature changes become less important.

Since all the adsorbents used were found to catalyze ortho-para conversion, the calibrations were carried out with hydrogen which had previously been equilibrated over charcoal at the temperature to be used. An increase of 1% in para-hydrogen content was found to correspond to a decrease of 0.1% in deuterium concentration. Ortho-para deuterium conversion is small at the adsorption temperatures used and the difference in heat capacity at room temperature negligible (13). No change in the conductivity readings could therefore be detected. Prior to a series of runs each adsorbent was tested for possible preferential adsorption of ortho-hydrogen as suggested in a number of recent papers (5, 18, 19). A charge of pure equilibrated hydrogen was fractionally desorbed and the fractions analyzed. Conductivity measurements in all cases agreed within $\pm 0.02\%$ in terms of deuterium content. A number of tests were also made to establish the absence of catalytic HD-formation. It can be shown from calculations made by Trenner (16) that the formation of 1% HD from an equimolar mixture of hydrogen and deuterium should cause a change in conductivity reading corresponding to about 0.1% D₂. Mixtures of the isotopes were accordingly left in contact with various parts of the apparatus for a period of 12 hours. No change in the conductivity readings was observed. This is in agreement with the results reported by Gould *et al.* (8), who tested mercury, activated charcoal, and glass surfaces for possible catalytic effects. Burstein (20), however, has found rapid conversion of hydrogen and deuterium to occur on charcoal previously evacuated for 1 month at 950° C. The effect was attributed to the baring of active spots. As a precaution all the adsorbents used in this work were evacuated for no longer than 24 hours at a temperature of 180–200° C.

Materials Used

Deuterium.—Supplied by Stuart Oxygen Co., San Francisco. Purity better than 99.5%; used without further purification.

Hydrogen.—Supplied by Dominion Oxygen Co., Toronto. Purified over charcoal at liquid air temperature.

Helium.—Supplied by Dominion Oxygen Co., Toronto. Used without further purification in dead-space determination.

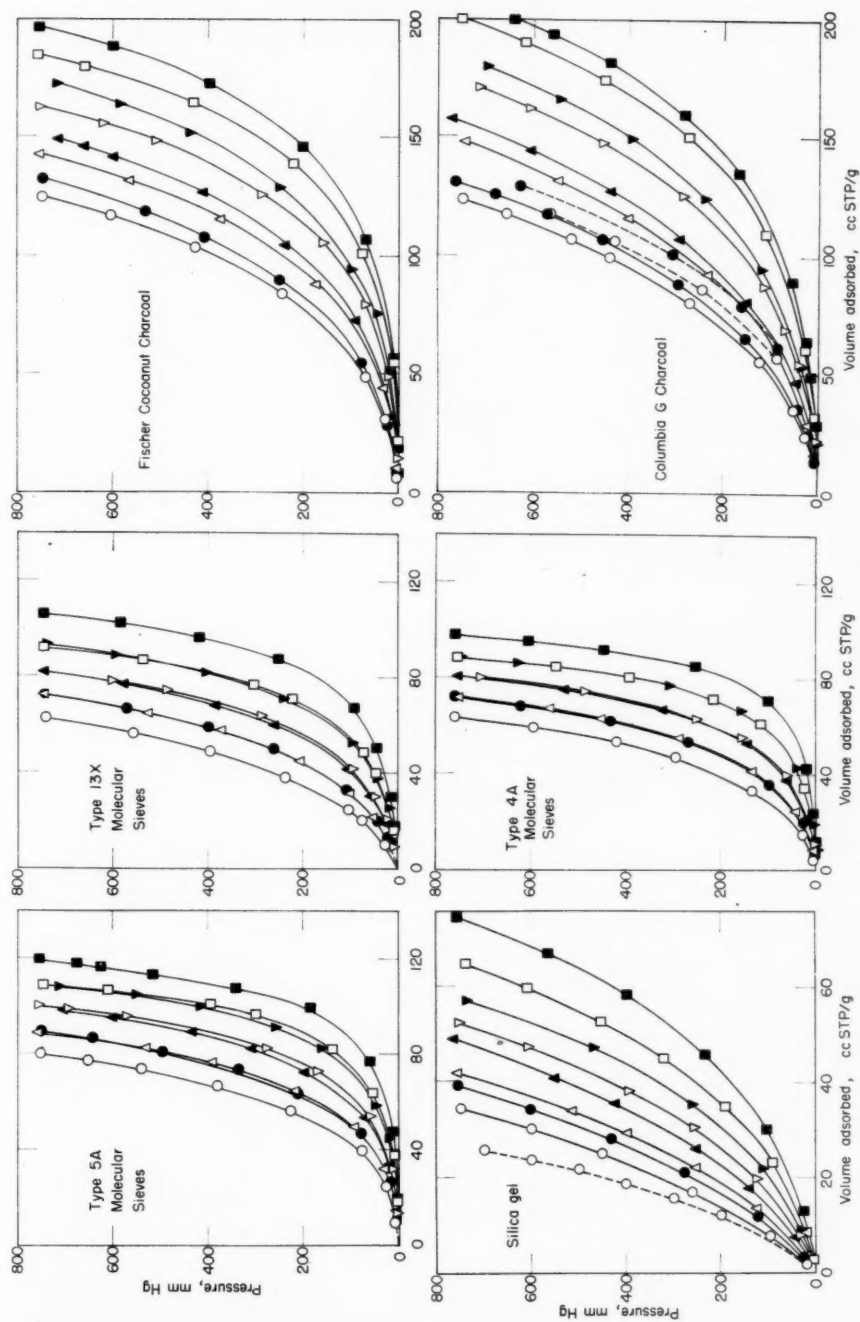


FIG. 3. Single component adsorption isotherms. Open symbols are for H_2 , closed for D_2 . Temperature ($^{\circ}K$) for \circ and \bullet , 75; \triangle and \blacktriangle , 80; \square and \blacksquare , 85; ∇ and \blacktriangledown , 90; Δ and \blacktriangleleft , 95. --- Ref. 22 (charcoal) and Ref. 23 (silica gel).

Adsorbents.—Columbia 'G' Charcoal, 12–20 mesh, 1250 sq. m/g, Carbide and Carbon Chemicals Co., New York. Fischer Coconut Charcoal, 12–20 mesh, 1100 sq. m/g. Supplied by Fischer Scientific Co., Toronto. Silica gel, 6–16 mesh, 750 sq. m/g, Fischer Scientific Co., Toronto. Molecular sieves type 4A, 5A, and 13X, 1/16-inch pellets containing approximately 20% inorganic binder, all 700–800 sq. m/g. Supplied by Linde Air Products Co., Tonawanda, N.Y.

Approximate formulae (21).—Type 4A: $0.96 \text{ Na}_2\text{O} \cdot 1.00 \text{ Al}_2\text{O}_3 \cdot 1.92 \text{ SiO}_2 \cdot x\text{H}_2\text{O}$
Type 13X: $0.83 \text{ Na}_2\text{O} \cdot 1.00 \text{ Al}_2\text{O}_3 \cdot 2.48 \text{ SiO}_2 \cdot x\text{H}_2\text{O}$. Type 5A is produced from type 4A through ion exchange of about 75% of the sodium ions by calcium ions. For a discussion of molecular sieve crystal structure, see Barrer (25).

Thermistors.—Type A33 matched thermistors, 2000-ohm nominal resistance. Supplied by Victory Engineering Corporation, Union, N.J.

RESULTS

Pure component adsorption isotherms of hydrogen and deuterium on the six adsorbents are shown in Fig. 3. Deuterium was found to be adsorbed to a greater extent than hydrogen in all cases investigated and both gases yield type I isotherms. The Freundlich and Langmuir equations were applied to the data but neither gave satisfactory agreement over the entire pressure range. The data of van Itterbeek and van Dingenen (22) (hydrogen and deuterium on "Carbotox" charcoal) and van der Waarden (23, hydrogen on silica gel) confirm the general trend of our isotherms.

Isosteric heats of adsorption were calculated from plots of $\log p$ versus $1/T$ at constant volume adsorbed. Straight lines were obtained in all cases over the entire temperature range. The heat of adsorption for deuterium was found to exceed that of hydrogen on all adsorbents, the difference tending to increase toward lower coverages (Fig. 4). The values found on charcoal compare well with the difference of 100 cal/mole calculated from the data of van Itterbeek and van Dingenen (22) and 80 cal/mole found by Beggerow (quoted by Melkonian and Repts (2)).

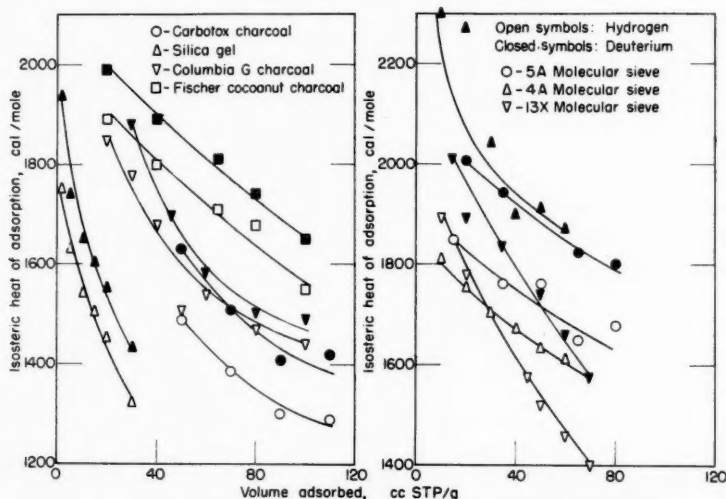
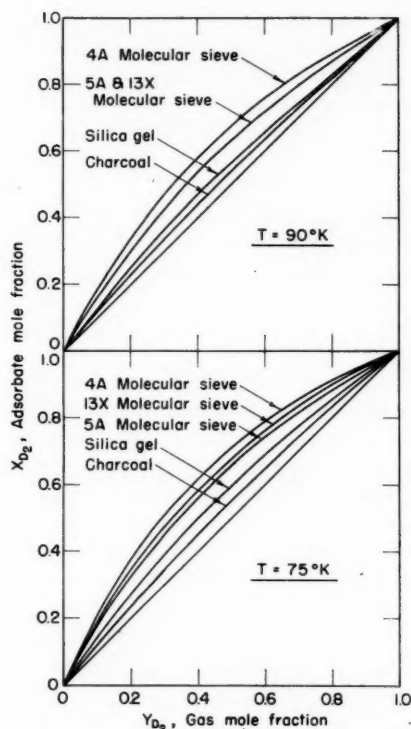


FIG. 4. Isosteric heats of adsorption of hydrogen and deuterium.

FIG. 5. Summary of binary adsorption equilibria ($\pi = 750$ mm Hg).

The binary data obtained in this work are summarized in Table II and Fig. 5. The results have been expressed in terms of the relative adsorptivity α which was found to be essentially constant over the entire concentration range investigated. More detailed graphs are given in Part II of this paper, where a comparison is made with values of α obtained directly from the single component data.

TABLE II
Summary of measured hydrogen-deuterium separation factor*

Adsorbent	$T = 90^\circ \text{K}$ $\pi = 750$ mm Hg	$T = 90^\circ \text{K}$ $\pi = 200$ mm Hg	$T = 75^\circ \text{K}$ $\pi = 750$ mm Hg
Columbia 'G' Charcoal	1.149 (± 0.013)	1.145 (± 0.004)	1.23 (± 0.013)
Fischer Coconut Charcoal	1.17 (± 0.008)	1.17 (± 0.011)	1.28 (± 0.013)
Silica gel	1.33 (± 0.023)	1.38 (± 0.029)	1.47 (± 0.097)
Type 4A molecular sieves	2.06 (± 0.12)	2.01 (± 0.10)	2.54 (± 0.07)
Type 5A molecular sieves	1.77 (± 0.12)	1.82 (± 0.18)	2.00 (± 0.18)
Type 13X molecular sieves	1.77 (± 0.08)	1.78 (± 0.015)	2.16 (± 0.10)

*Maximum deviations in parentheses.

A number of qualitative conclusions may be drawn from the results:

(1) There seems to be little variation in the separation factors measured on chemically identical adsorbents of different origin. Values determined by us on two different charcoals are nearly the same as that reported by Strange (4) on a sample of unidentified origin and, as will be shown in a subsequent paper (II), similar values can be derived from the single component data measured on Carbotox charcoal by van Itterbeek and van Dingenen (22) and on sugar charcoal by Barrer and Rideal (24).

(2) The relatively high separation factors obtained on the molecular sieves do not appear to be due to any screening effect of the pores. Type 13X sieves with a nominal pore diameter of 13 angstrom give similar enrichment as type 4A, the pore size of which is close to the van der Waals diameter of hydrogen (2.4 angstrom).^{*} A sample of 3A molecular sieves was also investigated but proved to have a negligible capacity for the two isotopes.

(3) The chemical composition of the adsorbent appears to have a marked effect on the separation factor, greater chemical heterogeneity tending to yield increased enrichment. The relative magnitude of α obtained on silica gel and charcoal agrees with the data of Melkonian and Repts (2), whose measurements at pressures of 1 micron Hg and less showed charcoal to be less effective than silica gel.

(4) The trend of increasing α with a decrease in temperature is confirmed by our results, but the lowest pressure used here (200 mm) was apparently not sufficiently small to reveal any effect on the separation factor.

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^{*}The van der Waals diameter of deuterium obtained from thermal conductivity and viscosity measurements at 20° C is identical with that of hydrogen (26 a, b).

ADSORPTION EQUILIBRIA OF HYDROGEN, DEUTERIUM, AND THEIR MIXTURES. PART II¹

D. BASMADJIAN²

ABSTRACT

An investigation has been made of the fundamental factors which determine isotope separation factors on adsorbents, based on hydrogen and deuterium isotherms reported in Part I. Through the use of a semiempirical thermodynamic approach, the binary separation factors α have been related to the single component isotherms ($p = f(v)$), and these in turn broken down into a number of terms involving the isosteric heat of adsorption q , temperature T , and surface coverage. If the less important contributions are neglected, the treatment leads to the following sequence of approximate relations:

$$[I] \quad \log \alpha \doteq \frac{1}{(v_{H_2})_\tau} \int_0^{(v_{H_2})_\tau} \log \left(\frac{p_{H_2}}{p_{D_2}} \right)_\tau dv \doteq \frac{0.11}{(v_{H_2})_\tau} \int_0^{(v_{H_2})_\tau} \frac{q_{D_2} - q_{H_2}}{T} dv \propto \frac{\epsilon_{H_2}^0 - \epsilon_{D_2}^0}{T} \quad [III]$$

[I]
[II]

where ϵ^0 = total vibrational zero-point energy of adsorbed molecules.

The rigorous form of equation [I] agrees well with the experimental results, and semi-quantitative agreement with the data is shown by equation [II]. A qualitative discussion of [III] is given. It is suggested that the horizontal zero-point vibrations of the adsorbed species in some cases constitute an important contributing factor in addition to the vertical vibrations previously thought to be solely responsible for differences in isotope behavior.

INTRODUCTION

In a previous paper (1) we had reported data obtained from measurements of binary and single component adsorption isotherms of hydrogen and deuterium on a number of adsorbents. The surprisingly high separation factors which were obtained, particularly on type 4A molecular sieves, have led us to examine the fundamental factors which determine adsorption equilibria involving isotopes.

Differences in the sorption of isotopes are frequently attributed solely to zero-point energy effects. Sherman and Eyring (2) derived the expression

$$[2] \quad \frac{r_{H_2}}{r_{D_2}} = e^{(q_{D_2} - q_{H_2})/RT} = e^{(\epsilon_{H_2}^0 - \epsilon_{D_2}^0)/RT},$$

where r = rate of desorption, to explain the deuterium enrichment obtained by Gould *et al.* (3) by desorption from charcoal. Barrer and Rideal (4) obtained linear isotherms for hydrogen and deuterium on charcoal at a few millimeters of Hg and expressed their results in terms of the equation

$$[3] \quad \left(\frac{p_{H_2}}{p_{D_2}} \right)_\tau = e^{(q_{D_2} - q_{H_2})/RT} = e^{(\epsilon_{H_2}^0 - \epsilon_{D_2}^0)/RT},$$

where p = equilibrium pressure, v = volume adsorbed.

A more quantitative approach is achieved by the use of partition functions, but the advantages of this method are offset by the assumptions which have to be made in formulating the energy states of the adsorbed phase. Wheeler (5) applied the method to single component equilibria of the isotopes, assuming the adsorbed molecules to be

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localized with 5 vibrational degrees of freedom relative to the surface. The result is described by the equation

$$[4] \quad \left(\frac{p_{H_2}}{p_{D_2}} \right)_v = \frac{v_{mD_2} - v_{H_2}}{v_{mH_2} - v_{H_2}}$$

where v_m = monolayer volume.

In a recent note, White and Haubach (6) propose extending this treatment to the calculation of binary separation factors. The authors apparently assume Langmuir's mixed isotherm (7) to apply, postulating vertical vibrations as well as hindered rotation in the adsorbed phase. As a first approximation, zero-point energies only are considered, leading to qualitative agreement with some results obtained on alumina at 20° K.

One immediate difficulty in applying the above treatments arises from the fact that our data do not obey Langmuir's isotherm. Even if this were the case, it would not necessarily indicate that we are dealing with an energetically homogeneous surface justifying the use of the simple partition functions proposed by Wheeler, and White and Haubach. The formulation of more complex functions, on the other hand, would require a knowledge of surface energy distributions and other fundamental data which are difficult to obtain (see e.g. ref. 8). In the treatment given below we have sought to avoid these difficulties by employing a semiempirical thermodynamic approach involving variables which are easily obtained or estimated from the measured isotherms. The stepwise procedure consists in relating the binary separation factor α to the single component pressure ratio at constant volume adsorbed $(p_{H_2}/p_{D_2})_v$; this ratio is in turn expressed in terms of the difference in heat of adsorption of the two isotopes, system temperature, and surface coverage. The more significant of these, the heat of adsorption difference, is further broken down into the zero-point energies, adsorbent/adsorbate interaction potentials, and heat capacity integrals of the adsorbed isotopes. Each of these terms is discussed qualitatively as to its contribution to the total separation factor.

(a) Correlation of Binary and Single Component Data

Most theoretical treatments of this problem stipulate single component data which conform to a given isotherm equation, e.g., the Langmuir (7), Freundlich (9), or BET (10) isotherms. Our own data, which do not obey any of these equations, are represented by a modification of the correlation given by Lewis *et al.* (11):

$$[5] \quad \frac{(v_{H_2})_v(\alpha-1)}{\alpha(v_{H_2}/v_{D_2})_v-1} \log \alpha \left(\frac{v_{H_2}}{v_{D_2}} \right)_v = (v_{D_2} - v_{H_2})_v \log \pi + \int_0^{(v_{H_2})_v} \log p_{H_2} dv - \int_0^{(v_{D_2})_v} \log p_{D_2} dv.$$

The equation is based on the assumption that (a) α is independent of concentration, (b) the total binary adsorbate volume v_T is related to the adsorbate mole fraction X as follows:

$$[6] \quad \frac{1}{v_T} = \frac{X_{H_2}}{(v_{H_2})_v} + \frac{X_{D_2}}{(v_{D_2})_v}.$$

The first of these was found to hold in the region 10–90% D_2 and will be assumed valid over the entire concentration range. The second assumption can be shown by an appropriate plot to be a close approximation of the linear relation found experimentally for our system:

$$[7] \quad v_T = (v_{D_2} - v_{H_2})_v X_{D_2} + (v_{H_2})_v.$$

The derivation given by Lewis *et al.* was repeated using equation [7] instead of [6]. The result, although considerably more complex, was found to be fully equivalent to the Lewis correlation.

For the purposes of this work it was found best to combine the two single component integrals in equation [5] into the pressure ratio $(p_{H_2}/p_{D_2})_v$, the residual term being evaluated by assuming $\log p$ to vary linearly with v over the short range in question. Thus:

$$[8] \quad \frac{(\alpha-1)(v_{D_2}/v_{H_2})_\pi}{\alpha - (v_{D_2}/v_{H_2})_\pi} \log \frac{\alpha}{(v_{D_2}/v_{H_2})_\pi} = \frac{1}{(v_{H_2})_\pi} \int_0^{(v_{H_2})_\pi} \log \left(\frac{p_{H_2}}{p_{D_2}} \right)_v dv + \frac{1}{2} (v_{D_2}/v_{H_2} - 1)_\pi \log \left(\frac{p_{H_2}}{p_{D_2}} \right)_{(v_{H_2})_\pi}$$

It can be shown that for $\alpha < 4$ and $(v_{D_2}/v_{H_2})_\pi < 1.5$, the equation reduces to the approximate expression

$$[9] \quad \log \alpha \doteq \frac{1}{(v_{H_2})_\pi} \int_0^{(v_{H_2})_\pi} \log \left(\frac{p_{H_2}}{p_{D_2}} \right)_v dv.$$

Plots of the ratio $(p_{H_2}/p_{D_2})_v$ versus v for the single component data reported previously are presented in Fig. 1. The curves show an initial sharp drop and appear to pass through a minimum at higher pressures. The general trend of the curves is confirmed by the data of van Isterbeek and van Dingenen (12) for hydrogen and deuterium on "Carbotox" charcoal. In terms of equation [9] the plots of Fig. 1 predict an increase in the separation factor α with decreasing total pressure π and temperature. This is confirmed by the high separations obtained by various authors on silica gel and charcoal at extremely low pressures and temperatures (see Part I, Table I). Our own binary data generally show excellent agreement with values of α calculated from equation [8] (see Fig. 2). The deviations observed in the case of the 4A molecular sieves are partly due

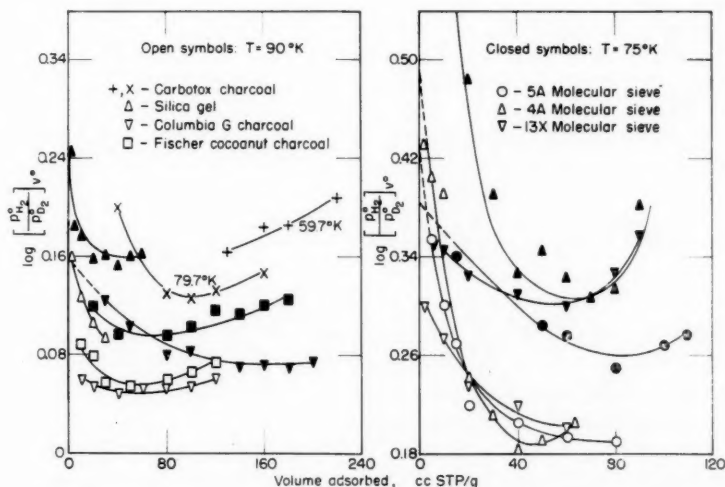


FIG. 1. Ratio of pure component adsorption pressure of hydrogen and deuterium versus volume adsorbed.

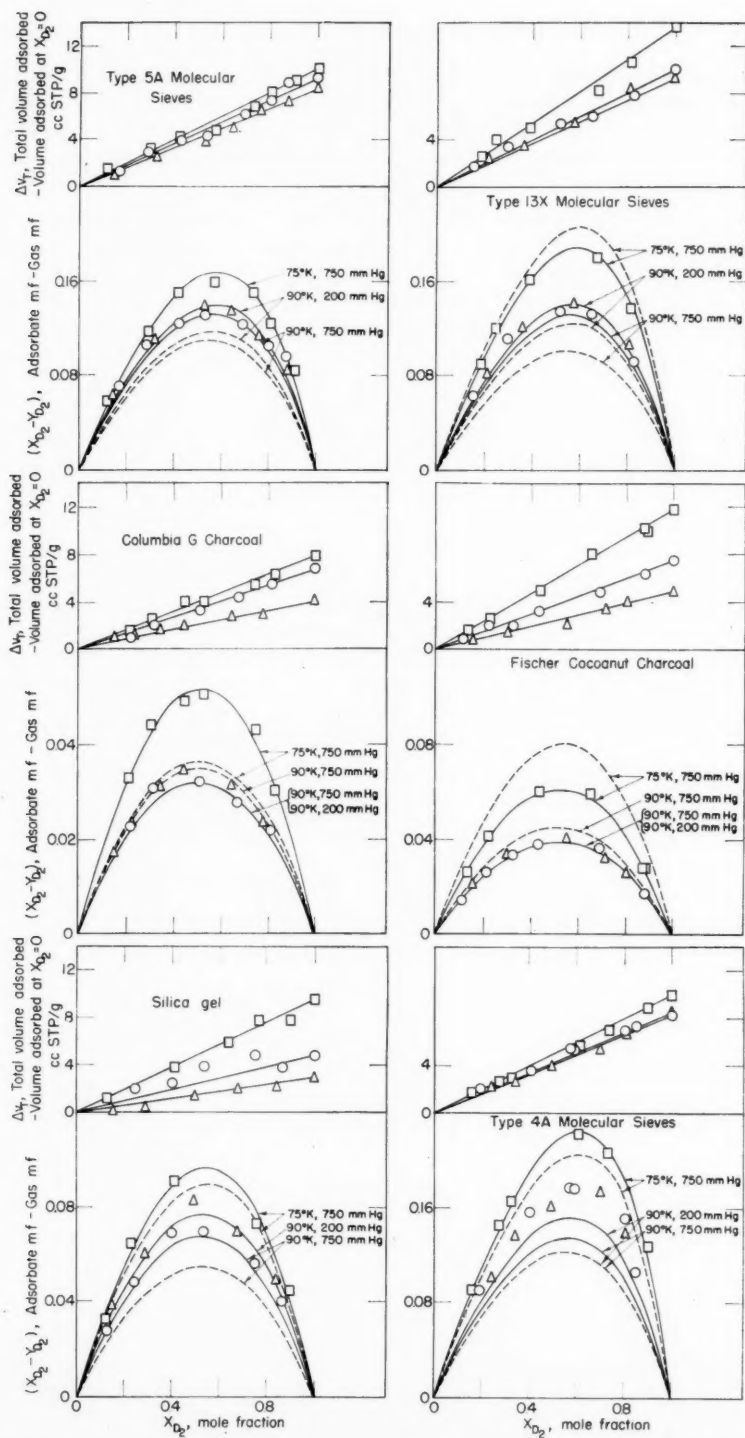


FIG. 2. Comparison of binary adsorption equilibria with equation [8] (—) and [9] (-----).
 \circ $T = 90^\circ\text{K}$ $\pi = 750\text{ mm Hg}$, \triangle $T = 90^\circ\text{K}$ $\pi = 200\text{ mm Hg}$, \square $T = 75^\circ\text{K}$ $\pi = 750\text{ mm Hg}$.

to the difficulty in extrapolating the pressure ratio to $v = 0$, and possibly also to a variation of α with composition at low concentrations.

Equation [9] is seen to be very similar to Raoult's Law for ideal liquid solutions, to which in fact it reduces by assuming p_{H_2}/p_{D_2} to be constant for all values of v . A slightly different form of this equation may be derived by postulating proportionality between gas and adsorbed phase mole fractions, Y and X , as follows:

$$[10] \quad \begin{aligned} Y_{D_2} \pi &= X_{D_2} (p_{D_2})_{v_T} \\ Y_{H_2} \pi &= X_{H_2} (p_{H_2})_{v_T} \end{aligned} \quad \text{whence} \quad \frac{Y_{H_2} \cdot X_{D_2}}{Y_{D_2} \cdot X_{H_2}} = \alpha = \left(\frac{p_{H_2}}{p_{D_2}} \right)_{v_T}.$$

Values of α obtained from equation [10] agree less well with the experimental results than those calculated from the more accurate equation [8] (see Fig. 2). This underlines the importance of making allowance for the variation in the pressure ratio $(p_{H_2}/p_{D_2})_v$ with coverage.

(b) *The Pure Component Pressure Ratio*

We next proceed to express the pure component equilibrium pressure in terms of conventional thermodynamic functions. In the first instance this leads to the equation

$$[11] \quad \Delta\mu = RT \ln p = \Delta H - T\Delta S.$$

(For an exact definition of the functions see, e.g., ref. 13a.)

The enthalpy term is in this case equivalent to the isosteric heat of adsorption q (13a), which is determined in the usual manner from a plot of $\log p$ versus $1/T$ at constant volume adsorbed. The entropy term is most conveniently evaluated by making use of a semiempirical correlation proposed by Everett (13b):

$$[12] \quad \Delta S = \Delta S^* - R \ln \frac{\theta}{1-\theta}$$

where

$$[13] \quad \Delta S^* = A \cdot q + B.$$

For a large number of gases on charcoal at 300° K, A was found to be equal to $0.38/T$ (14). Other systems give values of A between $0.45/T$ and $0.55/T$ (28), particularly at low temperatures, and a partial theoretical justification of this has been given by Drain and Morrison (14). Following Young (28), we have chosen the value of $0.50/T$ for A ; B appears to be essentially independent of temperature below 90° K (13b), although this conclusion is based on rather scant data. The isotope pressure ratio then becomes:

$$[14] \quad \log \left(\frac{p_{H_2}}{p_{D_2}} \right)_v = 0.11 \frac{q_{D_2} - q_{H_2}}{T} + \log \frac{v_{mD_2}/v_{mH_2} - \theta_{H_2}}{1 - \theta_{H_2}}$$

and

$$[15] \quad \log \alpha = \frac{0.11}{(v_{H_2})_v} \int_0^{(v_{H_2})_v} \frac{q_{D_2} - q_{H_2}}{T} dv + \frac{1}{(v_{H_2})_v} \int_0^{(v_{H_2})_v} \log \frac{v_{mD_2}/v_{mH_2} - \theta_{H_2}}{1 - \theta_{H_2}} dv.$$

A quantitative comparison with our data is rendered difficult by the high accuracy required in evaluating the heat of adsorption integral. Table I shows the results of some calculations based on approximate average values of $q_{D_2} - q_{H_2}$. The monolayer volume ratio was taken as 1.10 based on the low temperature isotherms of van Itterbeek and van Dingenen (12). Liquid molar volumes give a value of 1.20, solid molar volumes

one of about 1.15 (15). The pure component hydrogen coverage Θ_{H_2} was estimated from surface area measurements to vary from 0 to 0.3 for the cases investigated.

It is apparent that the term $(q_{D_2} - q_{H_2})/T$ constitutes the main contribution to the separation factor. Hence, as a first approximation:

$$[16a] \quad \log \alpha \doteq \frac{0.11}{(v_{H_2})_T} \int_0^{(v_{H_2})_T} \frac{q_{D_2} - q_{H_2}}{T} dv.$$

Equations of a similar form

$$[16b] \quad \alpha = A \cdot e^{\Delta q/RT}$$

have been suggested by several authors on a purely empirical basis (e.g. 16, 17). The experimental results of these workers are unfortunately difficult to interpret in terms of equations [14] and [15] due to the lack of data on single component isotherms.

(c) *The Heat of Adsorption Difference*

Having established that the separation factor is largely determined by the heat of adsorption difference, it is of interest to examine the factors which cause the large variation of $q_{D_2} - q_{H_2}$ on the various adsorbents investigated. The difference is conveniently broken down into a number of separate terms, following the treatment of Orr (18):

$$[17] \quad (q_{D_2} - q_{H_2})_T = \phi_{D_2} - \phi_{H_2} - (\epsilon_{D_2}^0 - \epsilon_{H_2}^0) - \int_0^T C_{a_{D_2}} dT + \int_0^T C_{s_{D_2}} dT + \int_0^T C_{a_{H_2}} dT - \int_0^T C_{s_{H_2}} dT$$

where ϕ = total interaction energy, C_a = adsorbate heat capacity, C_g = ideal gas heat capacity. Due to a lack of data, it is not possible to present more than qualitative conclusions on the contribution made by each term. Most authors are inclined to emphasize the importance of the zero-point energy difference. There is in fact some reason to believe that neither of the other two terms contributes appreciably to $q_{D_2} - q_{H_2}$. The intermolecular potentials of gaseous hydrogen and deuterium are known to be identical (19). Calculations based on the Kirkwood-Mueller equation (7) have shown the interaction potential of the isotopes with adsorbent surfaces to be nearly identical. Thus, as a first approximation, $\Delta\phi$ may be set = 0.

No measurements have been made of the heat capacities of either hydrogen or deuterium in the adsorbed state. A number of authors have, however, reported values for nitrogen (20, 22), oxygen (22), krypton (21), and argon (23) adsorbed on rutile over a temperature range extending from near 0° K to well above the normal boiling point. The results indicate that the difference of the heat capacity integrals

$$- \int C_a dT + \int C_g dT$$

for these gases does not exceed 100–200 cal/mole. On this basis, the algebraic sum of the isotopic heat capacity integrals (equation [17]) may be expected to be even smaller, if not completely negligible. At any rate, it would seem difficult to attribute heat of adsorption differences as high as 300 cal/mole solely to heat capacity effects.

(d) *The Zero-point Energy Difference*

The zero-point energy of a harmonic oscillator vibrating vertically to a surface is given by:

$$[18] \quad \epsilon_v^0 = \frac{Nh}{\pi} \left(\frac{\phi}{4mr_0^2} \right)^{\frac{1}{2}}$$

h = Planck's constant and N = Avogadro's constant, where r_0 = equilibrium distance from surface and m = mass of isotope. Hence,

$$[19] \quad q_{D_2} - q_{H_2} = \frac{N \cdot h}{2\pi} \left\{ \left(\frac{\phi_{H_2}}{2mr_{0H_2}^2} \right)^{\frac{1}{2}} - \left(\frac{\phi_{D_2}}{2mr_{0D_2}^2} \right)^{\frac{1}{2}} \right\}.$$

While the order of magnitude of this expression agrees well with observed values of the heat of adsorption difference, it is difficult to account for its large variation with adsorbent composition solely on the basis of equation [19]. This would require a change in ϕ and r_0 incompatible with observed heats of adsorption or intermolecular van der Waals distances. It appears likely that other modes of energy may be involved, such as zero-point vibrations parallel to the surface or hindered rotation (6). Hill (24) has derived the following expression for horizontal vibrations on a surface with sinusoidal potential gradient:

$$[20] \quad \epsilon_h^0 = Nh \left(\frac{V}{4ms^3} \right)^{\frac{1}{2}}$$

where V = maximum potential barrier, s = distance between potential minima.

Equations of similar form may be expected to hold for more complex surfaces.

In the case of charcoal at higher coverages, the horizontal contribution is probably negligible, calculations having yielded a surface potential periodicity for argon on graphite of only about 50 cal/mole (25). Silica gel has been shown to give lower surface diffusivities than charcoal, in spite of higher heats of adsorption on the latter (26). This is interpreted as proof that the former has higher surface heterogeneity, possibly due to its chemical structure, and horizontal zero-point vibrations may partly account for the higher α values observed.

Surface heterogeneity may also be used to explain in part the high separation factors measured on the molecular sieves. This may again be due to the presence of different types of atoms and ions in the adsorbent surface. In addition, however, it is to be expected that the small size of the intercrystalline voids (11Å diameter, ref. 27) in which the main adsorption occurs will cause a considerable increase of the horizontal potential barrier. The large enrichment factors obtained by Melkonian and Reps (17), and others, at extremely low pressures can be similarly accounted for if the adsorption sites at these coverages are visualized as very narrow cracks.

The contribution due to hindered rotation (vertically to the surface) has been discussed briefly by White and Haubach (6). The ortho-hydrogen enrichment in the adsorbed phase reported by various authors (see Part I) indicates that the adsorbed

TABLE I
Qualitative test of equation [15] (π = 750 mm Hg)

Adsorbent	$q_{D_2} - q_{H_2}$	(log α) ^a calc.		(log α) exp.	
		$T = 90^\circ$	$T = 75^\circ \text{ K}$	$T = 90^\circ$	$T = 75^\circ \text{ K}$
Columbia Charcoal	50	0.11	0.12	0.055	0.089
Fisher Coconut Charcoal	75	0.14	0.16	0.068	0.11
Silica gel	100	0.17	0.20	0.12	0.17
Type 4A molecular sieves	300	0.42	0.49	0.32	0.40
Type 5A molecular sieves	150	0.23	0.27	0.25	0.30
Type 13X molecular sieves	175	0.26	0.31	0.25	0.33

^alog $(v_{mD_2}/v_{mH_2} - \theta_{H_2})/(1 - \theta_{H_2})$ varies from 0.04 to 0.06 for $\theta_{H_2} = 0$ to 0.3. An average value of 0.05 was used in all calculations.

isotopes do in fact possess some form of hindered rotational motion. It would be difficult, however, to explain the observed variation of $q_{D_2} - q_{H_2}$ with adsorbent composition solely on this basis, since this would again require a change in r_0 or the vertical potential barrier incompatible with the physical facts. The measurement of surface diffusivities suggests itself as a possible means for confirming the importance of surface heterogeneity, as compared to potential barriers affecting the vertical rotation of the molecule.

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IODINE COMPLEXES IN INERT SOLVENTS

XI. CRYOSCOPIC STUDY OF THE IODINE-NAPHTHALENE COMPLEX DISSOLVED IN CYCLOHEXANE¹

P. A. D. DE MAINE AND P. J. SANTIAGO

ABSTRACT

Here is reported cryoscopic evidence of the specific interaction between naphthalene and iodine dissolved together in cyclohexane. Cryoscopic constants accurate to within 2% are given for iodine and naphthalene dissolved separately in cyclohexane or in benzene.

INTRODUCTION

Since publication of the work of Benesi and Hildebrand (2), many researchers have used their spectrophotometric method, or modifications like those proposed by Ketelaar *et al.* (9) or Andrews and Keefer (1), to show that iodine molecules react reversibly with many aromatic and aliphatic compounds to form one-to-one complexes in solution. In many cases, the spectrophotometric method has been used to determine the heats of formation of these complexes. However, except for the calorimetric work reported by Hartley and Skinner (7) and the determination of solubilities by Kortüm and Vogel (10) there appears to be no direct non-spectrophotometric evidence of specific interaction between iodine and aromatic molecules in solution.

De Maine and Peone (4) have reported that the heat of formation ($\Delta H = -1.63 \pm 0.25$ kcal/mole) of the complex, naphthalene-I₂, is independent of the inert diluent used. Solvents used were carbon tetrachloride, cyclohexane, *n*-heptane, *n*-hexane, and chloroform.

In the present work we report cryoscopic evidence for the specific interaction between naphthalene and iodine in cyclohexane.

EXPERIMENTAL

(i) Chemicals

Fisher reagent grade anhydrous magnesium sulphate was heated for 6 hours at 150° C. Mallinckrodt A.R. grade benzene and Fisher spectrograde cyclohexane were stored in glass-stoppered bottles containing magnesium sulphate for at least 1 week before use. Solvents were removed with a "propipette" from the storage bottles immediately before the start of the experiment.

Fisher resublimed iodine and certified reagent grade naphthalene were used without further purification.

(ii) Procedure

Before each experiment the cell and its glass attachments (described below) were soaked in concentrated nitric acid for at least 6 hours, then were washed with copious amounts of water, and finally were rinsed with anhydrous acetone or methanol. Then the clean cell and attachments were heated at 55–65° C for not less than 1 hour and then were blown with pure nitrogen (dew point less than -40° C). Twenty-five milliliters of the anhydrous solvent was pipetted into the assembled cell, which was placed in the modified, Precision Scientific Co., cryoscopic molecular weight apparatus. The Beckman

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Differential thermometer was transferred from an ice-water bath to the cell after the solvent was cool. Care was taken to avoid transfer of moisture. The freezing point of the solvent was determined by the procedure described in the operating instructions of Precision Scientific Co. (3737 Cortland St., Chicago 47, Illinois. Index TS-65920-1). Special care was taken to maintain a constant tube-stirrer velocity, to cool at a rate less than 0.1°C per minute, and to seed the solution at a fixed temperature below the freezing point. The maximum amount of supercooling permissible for each solution was determined separately.

The freezing point of each aliquot of solvent was determined at least three times. Then the solution was heated approximately four degrees centigrade above the freezing point, and an accurately weighed portion of the desired solid was introduced into the cell by means of a polyethylene, long-stemmed funnel and an adapted Burgess Vibra-Tool. One hour after addition of the solid the new freezing point was determined. (In separate experiments we have shown that all the iodine and naphthalene were dissolved in both solvents within 45 minutes.) This procedure was repeated with further addition of the solid materials.

All the operations described above were performed in a dry, cool atmosphere (relative humidity less than 20%, temperature 15°C), and precautions were taken to exclude moisture from the freezing solutions at all times. The relative freezing point could be reproduced to within 0.001°C .

(iii) Instrumentation

(a) Description of Cell and Attachments

The cell supplied by the manufacturers was replaced by one modified as follows. The stainless-steel tube-stirrer and brass stirrer-bearing were replaced by an all-glass assembly, which was fitted with a CaCl_2 drying tube. The thermometer was replaced by a Beckman Differential thermometer fitted with a male 24-40 ground glass joint, and an electromagnetic vibrator clamped to the metal ferrule. The vibrator was switched on a few minutes before measurement of the freezing point in order to obtain the quoted accuracy (within 0.001°C). We also found that glass dust from the stirrer-bearing could effect changes as large as 0.010°C over several hours. Special design of the stirrer assembly and lubricating techniques was necessary to eliminate this source of error.

(b) Modifications of the Precision-shell, Cryoscopic Molecular Weight Apparatus

To insure continuous operation of the instrument for periods up to 24 hours, modifications were made as follows. The small-bore, copper cooling-coil which surrounds the cell cavity and is immersed in the coolant was replaced by a cooling-coil made of $\frac{3}{8}$ -inch internal diameter copper tubing. Ice water was pumped with a high capacity pump (greater than 1 gallon per minute) through the cooling-coil from a 5-gallon bath equipped with a high speed stirrer. The ice-bath pump and cooling-coil feed tubes were thoroughly insulated to minimize condensation. The coolant was commercial "Antifreeze".

RESULTS

More than 120 freezing points were each determined in duplicate with the instrument and procedure described above. With proper precautions to prevent moisture contamination of the solutions or hysteresis of the mercury in the Beckman Differential thermometer (13), the freezing points could be easily determined to within 0.001°C . The reproducibility obtained by us is considerably better than the 0.005°C quoted by the manufacturers (13).

In other experiments we have shown that the freezing point for solutions with single or mixed solutes does not change measurably even after several hours. The freezing points of fresh portions of each pure solvent did not vary by more than 0.002° C.

Cryoscopic constants (K_f = ° C for 1 mole dissolved in 100 g) for both solutes dissolved in each solvent were calculated with the standard formula (5). In these calculations the exact weights of solvent used were computed with densities estimated from published temperature-density equations (8). Such calculations have shown that K_f can be determined to high precision with small weights of the solute (Table I).

Typical data and K_f values for naphthalene dissolved separately in solutions of iodine plus cyclohexane are given in Table II.

TABLE I

Cyclohexane						Benzene					
Iodine			Naphthalene			Iodine			Naphthalene		
w (g)	Δt° C	K_f	w (g)	Δt° C	K_f	w (g)	Δt° C	K_f	w (g)	Δt° C	K_f
0.0315	0.109	170.1	0.0573	0.499	217.3	0.1040	0.066	35.4	0.1295	0.236	51.3
0.0279	0.094	165.7	0.0636	0.569	223.2	0.1051	0.063	33.5	0.1009	0.187	52.2
0.0323	0.111	169.2	0.0498	0.439	220.0	0.1015	0.063	35.0	0.1036	0.184	50.0
0.0447	0.154	170.1	0.1209	1.068	220.4	0.1031	0.064	35.0	0.1027	0.190	52.1
0.0276	0.093	166.0	0.1707	1.507	220.0	0.2087	0.129	34.5	0.1049	0.194	52.1
0.0723	0.252	171.8	0.0558	0.481	215.1	0.3127	0.195	34.8	0.1066	0.189	49.9
0.0331	0.112	168.4	0.0470	0.408	216.6	0.4178	0.258	34.5	0.2386	0.445	52.5
0.0281	0.101	178.8	0.1028	0.889	215.8	0.5226	0.319	34.1	0.2045	0.371	51.1
						0.6241	0.382	34.2	0.3072	0.561	51.4
0.0247	0.088	176.1				0.7272	0.446	34.2	0.4121	0.755	51.6
0.0420	0.142	167.7							0.5187	0.944	51.3
0.0671	0.242	178.8									
0.0723	0.247	168.5									
0.0603	0.205	167.5									
Arithmetic mean		171.1			218.6			34.5			51.4
Square root-mean square deviation		4.3			2.4			0.5			0.8

NOTE: Cryoscopic constants (K_f) for iodine and naphthalene dissolved separately in cyclohexane or in benzene. Δt° C is the measured depression of the freezing point of the pure solvent by the indicated weight (w (g)) of solute added to 25 cc of solvent. The units for K_f are degrees centigrade for 1 mole of solute added to 100 g of solvent.

TABLE II

w_{I_2} (g)	w_N (g)	Δt° C	K_f	w_{I_2} (g)	w_N (g)	Δt° C	K_f
0.0289	—	0.000	—	0.0723	—	0.000	—
0.0289	0.0493	0.402	202.5	0.0723	0.0557	0.444	198.4
0.0315	—	0.000	—	0.0723	0.1040	0.831	198.0
0.0315	0.0608	0.502	204.8	0.0723	0.1632	1.292	197.0
0.0315	0.1206	1.011	207.8	0.0723	0.2147	1.681	194.7
0.0315	0.1789	1.482	205.4	0.0723	0.2778	2.146	191.1
0.0315	0.2351	1.932	203.8	0.0723	0.3290	2.523	190.7

NOTE: Cryoscopic constants (K_f) for naphthalene dissolved in iodine plus cyclohexane. Δt° C is the depression of the freezing point of the iodine solution observed on addition of the indicated weight of naphthalene (w_N (g)) to 25 cc of the pure solvent with w_{I_2} g of iodine. K_f is in degrees centigrade for 1 mole dissolved in 100 g of solvent. K_f for naphthalene alone is 218.6.

DISCUSSION

The new K_f value for naphthalene dissolved in benzene (51.4 ± 0.7) is in good agreement with the accepted value of 51.2 (6, 11). However, the new value of K_f for cyclohexane (218.6 ± 2.4) is significantly larger than the published values of 200 to 204 (6, 8, 11). The significantly lower K_f values reported for iodine in both solvents (Table I) cannot be

attributed to partial polymerization of the solute, as has been suggested for other compounds in cyclohexane (12), because the K_t values are independent of the iodine concentration (Table I). Thus these low K_t values must be due to formation of solid solutions (5).

The significant decrease observed in the K_t values for naphthalene for the mixed-solute system (Table II) cannot be attributed to "salting-out" of either component because absorption spectra of these solutions show no sudden break when the temperature is lowered to near the freezing point. Also the saturation concentrations for both components dissolved separately in the pure solvent are significantly greater than the concentrations we studied. Thus the observed decrease for K_t must be due to specific interactions between iodine and naphthalene molecules in solution. This conclusion is in accord with published spectrophotometric work (3, 4, 14).

Calculations with data for naphthalene dissolved in iodine plus benzene solutions show that K_t decreases only slightly in the presence of iodine. (The maximum decrease observed was 2.5 for 0.7000 g of naphthalene dissolved in 21.98 g of benzene and 0.3000 g of iodine.) Calculations with spectrophotometrically determined values for the equilibrium constants for the separate reactions between iodine and benzene (2) or naphthalene (3, 14) show that in the competitive system less than 2% of the iodine will combine with the naphthalene. Thus the small decrease in K_t values can be understood.

No attempt has been made to calculate the equilibrium constant and hence ΔH for the reaction between iodine and naphthalene because of the different K_t values for iodine and naphthalene in cyclohexane.

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CALCULATION OF HEATS OF SOLUTION IN SATURATED MIXED ELECTROLYTES¹

Y. IYENGAR²

ABSTRACT

Theoretical equations have been derived for calculating heats of solutions of an electrolyte in its saturated system comprising one or more electrolytes. These expressions involve the application of "Harned's rule" concerning activity coefficients in mixed electrolytic solutions to an extension of van't Hoff's equation dealing with the temperature coefficient of solubility product in non-ideal systems. The commonly occurring case of mixed electrolytic pairs has been considered in detail. Application of theoretical equations to calculate the heats of solutions KCl, NaCl, and KNO₃ in the saturated systems KCl-NaCl-H₂O and KCl-KNO₃-H₂O is briefly discussed.

I. INTRODUCTION

A knowledge of the heats of solution of an electrolyte in its saturated system comprising one or more co-solutes is very useful in the computation of heat balances in processes involving steps such as the dissolution and crystallization of the electrolyte in these systems. Particularly of interest is the fact that the heat of crystallization of a salt is identified with its negative heat of solution at saturation.

Experimental data on heats of solutions in saturated solutions of mixed electrolytes are conspicuous by their absence. Even the data in fairly concentrated solutions are scarce (1-3). Such measurements are extremely difficult and tedious owing to the very slow rate of dissolution of a solute in a nearly saturated solution.

By a thermodynamic treatment involving the extension of van't Hoff's equation to non-ideal solutions, Williamson (4) derived expressions for calculating heats of solution of electrolytes at saturation in water. However, the influence of the presence of other electrolytes was not considered in his work.

The present work offers a theoretical method of calculating the heats of solution of a salt in saturated mixed electrolyte systems. The lack of experimental data in such systems lends considerable value to the theoretical solution.

II. GENERAL EQUATION FOR A PAIR OF ELECTROLYTES

(a) No Common Ions

Consider a system comprising a saturated solution of a pair of electrolytes having no ions in common between them. Let the properties of the species A and B be designated by the subscripts "1" and "2". The problem now is to derive expressions for evaluating heats of solutions of either A or B in a solution saturated with respect to both A and B.

From solubility relationships for component A

$$[1] \quad P_1 \gamma_1^{\nu_1} = P_{1(w)} \gamma_{1(w)}^{\nu_1}$$

where $P_{1(w)}$ and P_1 are the stoichiometrical solubility products of electrolyte A in water and in a solution saturated with respect to both A and B respectively, and $\gamma_{1(w)}$ and γ_1 are the corresponding mean activity coefficients. ν_1 is the total number of ions in 1 molecule of the electrolyte A.

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Extending van't Hoff's equation to non-ideal systems of component A in the saturated A-B-H₂O system,

$$[2] \quad \frac{d \ln P_1 \gamma_1^{\nu_1}}{dT} = \frac{\Delta H_{1(0)}}{RT^2},$$

where $\Delta H_{1(0)}$ is the differential heat of solution of A in pure water. Now, in the absence of a common ion,

$$[3] \quad P_1 = (\nu_+^{\nu_+} \nu_-^{\nu_-}) m_1^{\nu},$$

where ν_+ and ν_- are the number of cations and anions respectively in 1 molecule of the electrolyte and m_1 is the molality of A. Combining eqs. [3] and [2]

$$[4] \quad \frac{d \ln m_1}{dT} + \left(\frac{d \ln \gamma_1}{dT} \right)_{\text{sat}} = \frac{\Delta H_{1(0)}}{\nu_1 RT^2},$$

where the subscript "sat" stands for "solution saturated with respect to both A and B".

Since the variation of γ_1 with temperature is also accompanied by changes in the ionic strengths μ_1 and μ_2 of A and B respectively,

$$\partial \ln \gamma_1 = \left(\frac{\partial \ln \gamma_1}{\partial T} \right)_{\mu_1, \mu_2} dT + \left(\frac{\partial \ln \gamma_1}{\partial \mu_1} \right)_{\mu_2, T} d\mu_1 + \left(\frac{\partial \ln \gamma_1}{\partial \mu_2} \right)_{\mu_1, T} d\mu_2,$$

whence

$$[5] \quad \left(\frac{d \ln \gamma_1}{dT} \right)_{\text{sat}} = \left(\frac{\partial \ln \gamma_1}{\partial T} \right)_{\mu_1, \mu_2} + \left(\frac{\partial \ln \gamma_1}{\partial \mu_1} \right)_{\mu_2, T} \frac{d\mu_1}{dT} + \left(\frac{\partial \ln \gamma_1}{\partial \mu_2} \right)_{\mu_1, T} \frac{d\mu_2}{dT}.$$

Now,

$$[6] \quad \left(\frac{\partial \ln \gamma_1}{\partial T} \right)_{\mu_1, \mu_2} = -\frac{\bar{L}_1}{\nu_1 RT^2},$$

where \bar{L}_1 is the relative partial molal heat content of A in a solution saturated with respect to both A and B. Combining eqs. [4], [5], and [6],

$$[7] \quad \frac{d \ln m_1}{dT} + \left(\frac{\partial \ln \gamma_1}{\partial \mu_1} \right)_{\mu_2, T} \frac{d\mu_1}{dT} + \left(\frac{\partial \ln \gamma_1}{\partial \mu_2} \right)_{\mu_1, T} \frac{d\mu_2}{dT} = \frac{(\Delta H_{1(0)} + \bar{L}_1)}{\nu_1 RT^2}.$$

The variation of activity coefficients of salts in mixed electrolytes has been extensively investigated by Harned (5). Harned's rule, which has been successfully applied to several electrolyte pairs, can be written in the present context as

$$[8a] \quad \ln \gamma_1 = \ln \gamma_{1(0)} - \alpha_1 \mu_2$$

$$[8b] \quad \ln \gamma_2 = \ln \gamma_{2(0)} - \alpha_2 \mu_1,$$

where α_1 , α_2 are constants at a given temperature, μ_1 , μ_2 are the ionic strengths of A and B, and $\gamma_{1(0)}$, $\gamma_{2(0)}$ are the activity coefficients of A and B in their respective solutions in water at the total ionic strength $\mu = (\mu_1 + \mu_2)$.

Using eq. [8a],

$$[9] \quad \left(\frac{\partial \ln \gamma_1}{\partial \mu_1} \right)_{\mu_2, T} = \left(\frac{\partial \ln \gamma_{1(0)}}{\partial \mu_1} \right)_{\mu_2, T} - \mu_2 \left(\frac{\partial \alpha_1}{\partial \mu_1} \right)_{\mu_2, T} = \left(\frac{\partial \ln \gamma_{1(0)}}{\partial \mu} \right)_T - \mu_2 \left(\frac{\partial \alpha_1}{\partial \mu} \right)_T.$$

Also

$$[10] \quad \left(\frac{\partial \ln \gamma_1}{\partial \mu_2} \right)_{\mu_1, T} = \left(\frac{\partial \ln \gamma_{1(0)}}{\partial \mu} \right)_T - \mu_2 \left(\frac{\partial \alpha_1}{\partial \mu} \right)_T - \alpha_1.$$

The activity coefficient $\gamma_{1(0)}$ of A in water at high ionic strengths (even exceeding the solubility of the salt in water) may be obtained by the empirical rule of Åkerlöf and Thomas (6), according to which

$$[11] \quad \ln \gamma_{1(0)} - \ln \gamma_{R(0)} = \beta_1 \mu,$$

where $\gamma_{R(0)}$ is the mean activity coefficient of a reference electrolyte, and β_1 is a constant at a given temperature. The above relationship has been confirmed (6) for various electrolytes in concentrated solutions even up to saturation. Hydrochloric acid is generally used as the reference solute (R) since its activity coefficient is known over a very wide range of concentration (3–16 *m*) (7).

Differentiation of eq. [11] with respect to μ gives,

$$[12] \quad \left(\frac{\partial \ln \gamma_{1(0)}}{\partial \mu} \right)_T = \left(\frac{\partial \ln \gamma_{R(0)}}{\partial \mu} \right)_T + \beta_1.$$

Substituting eqs. [9], [10], and [12] in eq. [7], and also using the mathematical identity,

$$[13] \quad \begin{aligned} \frac{d \ln m_1}{dT} &= \frac{1}{m_1} \frac{dm_1}{dT}, \\ \frac{1}{m_1} \frac{dm_1}{dT} + \frac{d\mu_1}{dT} & \left[\left(\frac{\partial \ln \gamma_{R(0)}}{\partial \mu} \right)_T + \beta_1 - \mu_2 \left(\frac{\partial \alpha_1}{\partial \mu} \right)_T \right] \\ & + \frac{d\mu_2}{dT} \left[\left(\frac{\partial \ln \gamma_{R(0)}}{\partial \mu} \right)_T + \beta_1 - \mu_2 \left(\frac{\partial \alpha_1}{\partial \mu} \right)_T - \alpha_1 \right] = \frac{(\Delta H_{1(0)} + \bar{L}_1)}{\nu_1 R T^2}. \end{aligned}$$

β_1 can be determined from eq. [11] if the activity coefficients of electrolyte A and the reference electrolyte R at the same ionic strengths are known. Accurate values of β_1 may be obtained by plotting $\ln \gamma_{1(0)} - \ln \gamma_{R(0)}$ against μ and evaluating β_1 as the slope of this line.

α_1 may be evaluated from solubility data as follows.

Equation [1] may be written in the form,

$$[14] \quad \ln P_1/\nu_1 + \ln \gamma_1 = \ln P_{1(W)}/\nu_1 + \ln \gamma_{1(W)}.$$

Substituting for

$$P_{1(W)} = (\nu_+^{\nu_+} \nu_-^{\nu_-}) m_{1(W)}^{\nu},$$

$$P_1 = (\nu_+^{\nu_+} \nu_-^{\nu_-}) m_1^{\nu},$$

$$\ln \gamma_{1(W)} = \ln \gamma_{R(W_1)} + \beta_1 \mu_{1(W)},$$

and for $\ln \gamma_1$ from eqs. [8a] and [11], where $m_{1(W)}$ is the solubility of A in water, and $\mu_{1(W)}$ the ionic strength of A at saturation in water, and $\gamma_{R(W_1)}$ is the activity coefficient of the reference electrolyte (R) at ionic strength $\mu_{1(W)}$, eq. [14] now becomes,

$$\ln m_1 + \ln \gamma_{R(0)} + \beta_1 \mu - \alpha_1 \mu_2 = \ln m_{1(W)} + \ln \gamma_{R(W_1)} + \beta_1 \mu_{1(W)},$$

whence

$$[15] \quad \alpha_1 = \frac{1}{\mu_2} [\ln (m_1/m_{1(W)}) + \ln (\gamma_{R(0)}/\gamma_{R(W_1)}) + \beta_1 (\mu - \mu_{1(W)})].$$

Extending van't Hoff's equation to the non-ideal system of component B in saturated A-B-H₂O, the following expression analogous to eq. [13] may be derived going through similar steps.

$$[16] \quad \frac{1}{m_2} \frac{dm_2}{dT} + \frac{d\mu_2}{dT} \left[\left(\frac{\partial \ln \gamma_{R(0)}}{\partial \mu} \right)_T + \beta_2 - \mu_1 \left(\frac{\partial \alpha_2}{\partial \mu} \right)_T \right] + \frac{d\mu_1}{dT} \left[\left(\frac{\partial \ln \gamma_{R(0)}}{\partial \mu} \right)_T + \beta_2 - \mu_1 \left(\frac{\partial \alpha_2}{\partial \mu} \right)_T - \alpha_2 \right] = \frac{(\Delta H_{2(0)} + \bar{L}_2)}{\nu_2 RT^2},$$

where ν_2 is the total number of ions in 1 molecule of electrolyte B, and where β_2 , α_2 , $\Delta H_{2(0)}$, and \bar{L}_2 of B correspond to β_1 , α_1 , $\Delta H_{1(0)}$, and \bar{L}_1 of A.

β_2 and α_2 are given by expressions similar to eqs. [11] and [15]:

$$[17] \quad \ln \gamma_{2(0)} / \ln \gamma_{R(0)} = \beta_2 \mu$$

$$[18] \quad \alpha_2 = \frac{1}{\mu_1} [\ln (m_2/m_{2(W)}) + \ln (\gamma_{R(0)}/\gamma_{R(W_2)}) + \beta_2(\mu - \mu_{2(W)})].$$

Further simplifications of eqs. [13] and [16] are possible by considering certain relationships between α_1 and α_2 .

Harned and Owen (5) applied the Gibbs-Duhem equation to their rule (eqs. [8a], [8b]) and obtained, on the basis of Åkerlöf and Thomas' rule, eq. [11],

$$[19] \quad \alpha_1 - \alpha_2 = \text{constant},$$

whereas Glueckauf, McKay, and Mathieson (8, 9) obtained by thermodynamic considerations,

$$[20] \quad \alpha_1 + \alpha_2 = \text{constant}.$$

Equations [19] and [20] reveal that both α_1 and α_2 are constants independent of ionic strength of solution in concentrated solutions where Harned's rule is applicable. Since α_1 and α_2 are independent of μ ,

$$(\partial \alpha_1 / \partial \mu)_T = 0,$$

and

$$(\partial \alpha_2 / \partial \mu)_T = 0,$$

whence eq. [13] becomes

$$[21] \quad \frac{1}{m_1} \frac{dm_1}{dT} + \frac{d\mu_1}{dT} \left[\left(\frac{\partial \ln \gamma_{R(0)}}{\partial \mu} \right)_T + \beta_1 \right] + \frac{d\mu_2}{dT} \left[\left(\frac{\partial \ln \gamma_{R(0)}}{\partial \mu} \right)_T + \beta_1 - \alpha_1 \right] = \frac{(\Delta H_{1(0)} + \bar{L}_1)}{\nu_1 RT^2}$$

and eq. [16] becomes

$$[22] \quad \frac{1}{m_2} \frac{dm_2}{dT} + \frac{d\mu_2}{dT} \left[\left(\frac{\partial \ln \gamma_{R(0)}}{\partial \mu} \right)_T + \beta_2 \right] + \frac{d\mu_1}{dT} \left[\left(\frac{\partial \ln \gamma_{R(0)}}{\partial \mu} \right)_T + \beta_2 - \alpha_2 \right] = \frac{(\Delta H_{2(0)} + \bar{L}_2)}{\nu_2 RT^2}.$$

Denoting the left-hand sides of eqs. [21] and [22] by X and Y respectively, the equations can be rewritten as

$$[23] \quad \nu_1 RT^2 X = \Delta H_{1(0)} + \bar{L}_1$$

$$[24] \quad \nu_2 RT^2 Y = \Delta H_{2(0)} + \bar{L}_2.$$

Now, the heat of solution ΔH_{12} of A in a solution saturated with respect to both A and B is given by

$$\Delta H_{12} = (\bar{H}_{1(0)} - H_{1(s)}) - (\bar{H}_1 - \bar{H}_{1(0)}),$$

where $\bar{H}_{1(0)}$ is the partial molal enthalpy of A in an infinitely dilute solution of A in water, $H_{1(s)}$ is the molal enthalpy of A in the solid state, and \bar{H}_1 is the partial molal enthalpy of A in a solution saturated with respect to both A and B.

Since

$$(\bar{H}_{1(0)} - H_{1(s)}) = \Delta H_{1(0)}$$

and

$$(\bar{H}_1 - \bar{H}_{1(0)}) = \bar{L}_1,$$

therefore

$$[24a] \quad \Delta H_{12} = \Delta H_{1(0)} + \bar{L}_1$$

and similarly

$$[24b] \quad \Delta H_{21} = \Delta H_{2(0)} + \bar{L}_2,$$

where ΔH_{21} is the heat of solution of B in a solution saturated with respect to both A and B. Combining eqs. [23], [24], [24a], and [24b]

$$[25] \quad \Delta H_{12} = \nu_1 RT^2 X$$

$$[26] \quad \Delta H_{21} = \nu_2 RT^2 Y.$$

Equations [25] and [26] indicate that the heats of solutions of either one of the components in a solution saturated with respect to the electrolyte pair A, B can be simultaneously calculated by knowing X and Y from the solubility and thermodynamic data of the saturated system A-B-H₂O.

(b) Common Ion Effect

For the case of an electrolytic pair with a common ion eqs. [21] and [22] become slightly modified. If the anion is assumed to be common between the two electrolytes A and B, P_1 (see eq. [3]) is now given by

$$[27] \quad P_1 = m_+^{\nu_+} m_-^{\nu_-} = (\nu_+ m_1)^{\nu_+} (\nu_- m_1 + \nu_- m_2)^{\nu_-},$$

where ν_+ and ν_- are the number of cations and anions in 1 molecule of the electrolyte A respectively and ν_- is the number of anions in 1 molecule of B. Instead of eq. [4] we now have

$$[28] \quad \frac{1}{\nu_1} [\nu_+ d \ln m_1 / dT + \nu_- d \ln (\nu_- m_1 + \nu_- m_2) / dT] + (d \ln \gamma_1 / dT)_{\text{sat}} = \Delta H_{1(0)} / \nu_1 RT^2.$$

Equation [21] now becomes

$$[29] \quad \frac{1}{\nu_1} [\nu_- d \ln (\nu_- m_1 + \nu_- m_2) / dT + (dm_1 / dT) (\nu_+ / m_1)] + (d\mu_1 / dT) [(\partial \ln \gamma_{R(0)} / \partial \mu)_T + \beta_1] + (d\mu_2 / dT) [(\partial \ln \gamma_{R(0)} / \partial \mu)_T + \beta_1 - \alpha_1] = (\Delta H_{1(0)} + \bar{L}_1) / \nu_1 RT^2$$

and eq. [22] becomes

$$[30] \quad \frac{1}{\nu_2} \left[{}_{2\nu_-}d \ln ({}_{1\nu_-}m_1 + {}_{2\nu_-}m_2) / dt + \left(\frac{dm_2}{dT} \right) \left(\frac{{}_{2\nu_+}}{m_2} \right) \right] + \frac{d\mu_2}{dT} \left[\left(\frac{\partial \ln \gamma_{R(0)}}{\partial \mu} \right)_T + \beta_2 \right] \\ + \frac{d\mu_1}{dT} \left[\left(\frac{\partial \ln \gamma_{R(0)}}{\partial \mu} \right)_T + \beta_2 - \alpha_2 \right] = \frac{(\Delta H_{2(0)} + \bar{L}_1)}{\nu_2 R T^2}.$$

Also from eqs. [14] and [27],

$$[31] \quad \alpha_1 = \frac{1}{\mu_2} \left[\frac{{}_{1\nu_+}}{\nu_1} \ln m_1 + \frac{{}_{1\nu_-}}{\nu_1} \ln ({}_{1\nu_-}m_1 + {}_{2\nu_-}m_2) - \ln m_{1(W)} + \ln (\gamma_{R(0)} / \gamma_{R(W_1)}) \right. \\ \left. + \beta_1 (\mu - \mu_{1(W)}) \right].$$

Similarly,

$$[32] \quad \alpha_2 = \frac{1}{\mu_1} \left[\frac{{}_{2\nu_+}}{\nu_2} \ln m_2 + \frac{{}_{2\nu_-}}{\nu_2} \ln ({}_{1\nu_-}m_1 + {}_{2\nu_-}m_2) - \ln m_{2(W)} + \ln (\gamma_{R(0)} / \gamma_{R(W_2)}) \right. \\ \left. + \beta_2 (\mu - \mu_{2(W)}) \right].$$

ΔH_{12} and ΔH_{21} may be calculated as before, by substituting X and Y for the left-hand side of eqs. [29] and [30] and using the eqs. [25] and [26].

III. 1:1 ELECTROLYTE PAIR

Equations [21], [22], [29], and [30] become considerably simple for the case of a pair of 1:1 electrolytes.

(a) No Common Ion

Consider the case when the 1:1 electrolytes A and B have no ions in common. Equations [11], [15], [17], [18], [21], and [22] remain practically unchanged except that ionic strengths (μ) become molalities (m)

$$\mu = m, \quad \mu_1 = m_1, \quad \mu_2 = m_2,$$

$$\mu_{1(W)} = m_{1(W)}, \quad \mu_{2(W)} = m_{2(W)}.$$

Also

$$\nu = 2.$$

With these modifications and substitutions, ΔH_{12} and ΔH_{21} may be evaluated by eqs. [25] and [26].

(b) Common Ion Effect

Assume the anion to be common between the 1:1 electrolytes A and B. Since

$${}_{1\nu_-} = {}_{2\nu_-} = {}_{1\nu_+} = {}_{2\nu_+} = 1,$$

$$\mu_{1(W)} = m_{1(W)},$$

$$\mu_{2(W)} = m_{2(W)},$$

and

$$m = m_1 + m_2,$$

eqs. [29] and [30] become greatly simplified to

$$[33] \quad \left(\frac{dm_1}{dT}\right) \left[\frac{1}{2m_1} + \frac{1}{2m} + \left(\frac{\partial \ln \gamma_{R(0)}}{\partial m} \right)_T + \beta_1 \right] + \left(\frac{dm_2}{dT}\right) \left[\frac{1}{2m} + \left(\frac{\partial \ln \gamma_{R(0)}}{\partial m} \right)_T + \beta_1 - \alpha_1 \right] \\ = \frac{(\Delta H_{1(0)} + \bar{L}_1)}{2RT^2}$$

and

$$[34] \quad \left(\frac{dm_2}{dT}\right) \left[\frac{1}{2m_2} + \frac{1}{2m} + \left(\frac{\partial \ln \gamma_{R(0)}}{\partial m} \right)_T + \beta_2 \right] + \left(\frac{dm_1}{dT}\right) \left[\frac{1}{2m} + \left(\frac{\partial \ln \gamma_{R(0)}}{\partial m} \right)_T + \beta_2 - \alpha_2 \right] \\ = \frac{(\Delta H_{2(0)} + \bar{L}_2)}{2RT^2}$$

As before, the left-hand sides of these equations may be equated to X and Y respectively so that ΔH_{12} and ΔH_{21} may be evaluated from eqs. [25] and [26].

The expressions for α_1 and α_2 (eqs. [31] and [32]) also become greatly simplified to

$$[35] \quad \alpha_1 = (1/m_2) [\ln (m_1 m)^2 - \ln m_{1(W)} + \ln (\gamma_{R(0)}/\gamma_{R(W_1)}) + \beta_1 (m - m_{1(W)})]$$

$$[36] \quad \alpha_2 = (1/m_1) [\ln (m_2 m)^2 - \ln m_{2(W)} + \ln (\gamma_{R(0)}/\gamma_{R(W_2)}) + \beta_2 (m - m_{2(W)})].$$

The expressions for β_1 and β_2 are similar to eq. [11] with μ being equal to molality.

IV. APPLICATION OF THEORY TO EXPERIMENTAL RESULTS

The above theoretical treatment has been applied to the saturated KCl-NaCl-H₂O and KCl-KNO₃-H₂O systems for calculating heats of solutions of both salts in each of the saturated systems.

Since both these are 1:1 electrolyte systems with common ions, eqs. [33] and [34] along with eqs. [25] and [26] are to be applied for calculation of heats of solutions. The data and calculations are given in Tables I and II.

TABLE I
Data for the saturated systems KCl-NaCl-H₂O and KCl-KNO₃-H₂O

$t^\circ \text{C}$	m_1	m_2	dm_1/dT	dm_2/dT	$m_{1(W)}$	$m_{2(W)}$	$\ln \gamma_{R(W_1)}$	$\ln \gamma_{R(W_2)}$	$\ln \gamma_{R(0)}$
(i) KCl-NaCl-H ₂ O (subscript "1" refers to KCl and "2" to NaCl)									
18	1.93 ^a	5.16 ^a	.0319 ^a	-.0128 ^a	4.48 ^b	6.14 ^b	.737 ^c	1.264 ^c	1.568 ^c
25	2.17	5.08	.0336	-.0111	4.83	6.17	.803	1.216	1.550
40	2.69	4.94	.0336	-.0078	5.37	6.23	.857	1.108	1.503
(ii) KCl-KNO ₃ -H ₂ O (subscript "1" refers to KCl and "2" to KNO ₃)									
25	4.42 ^b	2.14 ^b	.0227 ^b	.0636 ^b	4.83 ^b	3.69 ^b	.803 ^c	.461 ^c	1.193 ^c

^aUnpublished results from Palestine Potash Co., Jerusalem, communicated by Dr. Martin Wilson, now with the U.S. Borax Research Corporation.

^bA. Seidell, Solubilities of inorganic and metal organic compounds. Vol. I. D. Van Nostrand Company, Inc., New York, 1940.

^cReference 5, p. 577.

V. DISCUSSION OF RESULTS

No experimental data are yet available on heats of solutions in nearly saturated salt pairs. However, the influence of added electrolytes on the heats of solutions of salts has been experimentally investigated (1, 2). Our calculations in saturated systems may be qualitatively reviewed in relation to the data in the unsaturated systems. Drucker's

TABLE II
Heats of solutions in the saturated systems KCl-NaCl-H₂O and KCl-KNO₃-H₂O

<i>t</i> ° C	β_1	β_2	α_1	α_2	$\Delta H_{1(0)}$	$\Delta H_{2(0)}$	ΔH_{12}	ΔH_{21}
(i) KCl-NaCl-H ₂ O (subscript "1" refers to KCl and "2" to NaCl)								
18	-.286 ^a	-.210 ^a	-.0206	.0461	4.44 ^b	1.28 ^b	3.33	0.19
25	-.275 ^c	-.198 ^c	-.0228 ^f	.0468 ^g	4.12 ^d	1.07 ^d	3.42	0.43
40	-.250 ^a	-.172 ^a	-.0182	.0532	3.68 ^e	0.68 ^e	3.34	0.73
(ii) KCl-KNO ₃ -H ₂ O (subscript "1" refers to KCl and "2" to KNO ₃)								
25	-.275 ^c	-.520 ^c	.0780	-.137	4.12 ^d	8.38 ^d	2.59	2.31

^aCalculated from interpolated data in reference 5, pp. 557, 558.

^bInternational Critical Tables. Vol V. Natl. Research Council U.S. 1929. pp. 200, 203.

^cCalculated from data tabulated by R. A. Robinson and R. H. Stokes. Trans. Faraday Soc. 45, 612 (1949).

^dReference 3.

^eN. K. Voskrenskaya and K. S. Ponomareva. Compt. rend. acad. sci. U.R.S.S. 45, 188 (1944).

^f $\alpha_1 = -.02$ and $\alpha_2 = .059$, at a total molality of 5, obtained from e.m.f. studies (reference 9, p. 179).

^g $\alpha_2 = .048$ from solubility studies of G. Åkerlöf. J. Phys. Chem. 41, 1053 (1937).

work on KCl-NaCl-H₂O system indicates that the heat of solution of KCl was depressed from 4.4 kcal/mole in water (18° C) to 3.2 kcal/mole on the addition of 4.0 molar NaCl. This depression of 1.2 kcal/mole may be compared with the value of \bar{L}_1 (eq. [23]) which represents the relative partial molal heat content of NaCl in a solution saturated with respect to both KCl and NaCl.

$$\begin{aligned}\bar{L}_1 &= 2RT^2X - \Delta H_{1(0)} \\ &= 3.33 - 4.44 = -1.11 \text{ at } 18^\circ \text{ C,}\end{aligned}$$

which is close to the observed depression. Since the system investigated by Drucker had about 0.2 molal KCl in it, it appears that \bar{L}_1 does not alter very much between this concentration and saturation (1.93 *m*). The data (2) on KCl-KNO₃-H₂O system are not extensive enough to evaluate heats of solutions at concentrations nearing saturation even by extrapolation. However, the high negative value of

$$\bar{L}_2 = 2RT^2Y - \Delta H_{2(0)} = -6.07 \text{ kcal/mole}$$

predicted by theory for a saturated KCl-KNO₃-H₂O system is justified by the trend of experimental results according to which (3) \bar{L}_2 in a solution containing 2.7 *m* KNO₃ and 0.27 *m* KCl is considerably large and negative ($\bar{L}_2 = 4.14 - 8.59 = -4.45$ kcal/mole).

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APPENDIX

Heats of Solutions in Saturated Multicomponent Systems

The present treatment may be extended to multicomponent systems as follows: Consider a saturated system of 'n' components A_1, A_2, \dots, A_n . Extending van't Hoff's equation with respect to component A_1 , whose properties are designated by subscript "1",

$$[A1] \quad d \ln P_1 \gamma_1^{r_1} / dT = \Delta H_{1(0)} / RT^2,$$

whence

$$[A2] \quad \frac{1}{\nu_1} \frac{d \ln P_1}{dT} + \left(\frac{d \ln \gamma_1}{dT} \right)_{\text{sat}} = \frac{\Delta H_{1(0)}}{\nu_1 RT^2}.$$

Now,

$$[A3] \quad \left(\frac{d \ln \gamma_1}{dT} \right)_{\text{sat}} = \left(\frac{\partial \ln \gamma_1}{\partial T} \right)_{\mu_1, \mu_2, \dots, \mu_n} + \left(\frac{\partial \ln \gamma_1}{\partial \mu_1} \right)_{\mu_2, \mu_3, \dots, \mu_n, T} \left(\frac{d\mu_1}{dT} \right) \\ + \left(\frac{\partial \ln \gamma_1}{\partial \mu_2} \right)_{\mu_1, \mu_3, \dots, \mu_n, T} \left(\frac{d\mu_2}{dT} \right) + \dots + \left(\frac{\partial \ln \gamma_1}{\partial \mu_n} \right)_{\mu_1, \mu_2, \dots, \mu_{n-1}, T} \left(\frac{d\mu_n}{dT} \right),$$

where $\mu_1, \mu_2, \dots, \mu_n$ are the ionic strengths of A_1, A_2, \dots, A_n respectively. Now, assuming validity of Harned's rule (see eqs. [8a], [8b] of text)

$$[A4] \quad \begin{aligned} \ln \gamma_1 &= \ln \gamma_{1(0)} - \alpha_1(\mu - \mu_1) \\ \ln \gamma_2 &= \ln \gamma_{2(0)} - \alpha_2(\mu - \mu_2) \\ \ln \gamma_n &= \ln \gamma_{n(0)} - \alpha_n(\mu - \mu_n), \end{aligned}$$

where μ , the total ionic strength $= (\mu_1 + \mu_2 + \dots + \mu_n)$. From [A4], equations analogous to [9] and [10] of text follow:

$$[A5] \quad \left(\frac{\partial \ln \gamma_1}{\partial \mu_1} \right)_{\mu_2, \mu_3, \dots, \mu_n, T} = \left(\frac{\partial \ln \gamma_{1(0)}}{\partial \mu} \right)_T - (\mu - \mu_1) \left(\frac{\partial \alpha_1}{\partial \mu} \right)_T$$

and

$$[A6_1] \quad \left(\frac{\partial \ln \gamma_1}{\partial \mu_2} \right)_{\mu_1, \mu_3, \dots, \mu_n, T} = \left(\frac{\partial \ln \gamma_{1(0)}}{\partial \mu} \right)_T - (\mu - \mu_1) \left(\frac{\partial \alpha_1}{\partial \mu} \right)_T - \alpha_1$$

$$[A6_n] \quad \left(\frac{\partial \ln \gamma_1}{\partial \mu_n} \right)_{\mu_1, \mu_2, \dots, \mu_{n-1}, T} = \left(\frac{\partial \ln \gamma_{1(0)}}{\partial \mu} \right)_T - (\mu - \mu_1) \left(\frac{\partial \alpha_1}{\partial \mu} \right)_T - \alpha_1.$$

Further,

$$[A7] \quad \left(\frac{\partial \ln \gamma_{1(0)}}{\partial \mu} \right)_T = \left(\frac{\partial \ln \gamma_{R(0)}}{\partial \mu} \right)_T + \beta_1$$

analogous to eq. [12] of text.

Substituting eqs. [A7], [A6₁]–[A6_n], and [A5] in eq. [A3] and also noting that

$$(\partial \alpha_1 / \partial \mu)_T = 0$$

and

$$\left(\frac{\partial \ln \gamma_1}{\partial T} \right)_{\mu_1, \mu_2, \dots, \mu_n} = - \frac{\bar{L}_1}{\nu_1 RT^2},$$

where \bar{L}_1 is the relative partial molal heat content of A_1 in the saturated multicomponent system,

$$[A8_1] \quad \frac{1}{\nu_1} \frac{d \ln P_1}{dT} + \frac{d\mu_1}{dT} \left[\left(\frac{\partial \ln \gamma_{R(0)}}{\partial \mu} \right)_T + \beta_1 \right] + \frac{d(\mu - \mu_1)}{dT} \left[\left(\frac{\partial \ln \gamma_{R(0)}}{\partial \mu} \right)_T + \beta_1 - \alpha_1 \right] = \frac{(\Delta H_{1(0)} + \bar{L}_1)}{\nu_1 RT^2}.$$

Equations similar to [A8₁] may be written for the other components. In general,

$$[A8_n] \quad \frac{1}{\nu_n} \frac{d \ln P_n}{dT} + \frac{d\mu_n}{dT} \left[\left(\frac{\partial \ln \gamma_{R(0)}}{\partial \mu} \right)_T + \beta_n \right] + \frac{d(\mu - \mu_n)}{dT} \left[\left(\frac{\partial \ln \gamma_{R(0)}}{\partial \mu} \right)_T + \beta_n - \alpha_n \right] = \frac{(\Delta H_{n(0)} + \bar{L}_n)}{\nu_n RT^2},$$

where, P_1, P_2, \dots, P_n are the stoichiometric solubility products and $\Delta H_{1(0)}, \Delta H_{2(0)}, \dots, \Delta H_{n(0)}$ are the differential heats of solutions in water of A_1, A_2, \dots, A_n respectively. A knowledge of $\beta_1, \beta_2, \dots, \beta_n$ and $\alpha_1, \alpha_2, \dots, \alpha_n$ is necessary to evaluate the left-hand sides of eqs. [A8₁] to [A8_n]. Now $\beta_1, \beta_2, \dots, \beta_n$ are given by the equations of the type,

$$[A9] \quad \ln \gamma_{n(0)} = \ln \gamma_{R(0)} + \mu \beta_n.$$

$\alpha_1, \alpha_2, \dots, \alpha_n$ are evaluated as follows.

For the species A_n , the solubility relationship gives

$$[A10] \quad \ln P_n / \nu_n + \ln \gamma_n = \ln P_{n(w)} / \nu_n + \ln \gamma_{n(w)}$$

where the subscript (w) indicates "solution in pure water". Substituting for $\ln \gamma_n$ from eqs. [A4] and [A9] and remembering that

$$\ln \gamma_{n(w)} = \ln \gamma_{R(w)} + \beta_n \mu_{n(w)},$$

where $\mu_{n(w)}$ is the ionic strength of A_n , we get on rearranging,

$$[A11] \quad \alpha_n = [(1/\nu_n) \ln (P_n/P_{n(w)}) + \ln (\gamma_{R(0)}/\gamma_{R(w)}) + \beta_n (\mu - \mu_{n(w)})] / (\mu - \mu_n).$$

Now, denoting the left-hand sides of eqs. [A8₁] to [A8_n] by X_1, X_2, \dots, X_n , respectively

$$[A12_1] \quad \nu_1 X_1 RT^2 = \Delta H_{1(0)} + \bar{L}_1$$

$$[A12_2] \quad \nu_2 X_2 RT^2 = \Delta H_{2(0)} + \bar{L}_2$$

$$[A12_n] \quad \nu_n X_n RT^2 = \Delta H_{n(0)} + \bar{L}_n.$$

Now, if $\Delta H_1, \Delta H_2, \dots, \Delta H_n$ are the heats of solutions of A_1, A_2, \dots, A_n , respectively, in a system saturated with all the components

$$[A13_1] \quad \Delta H_1 = \Delta H_{1(0)} + \bar{L}_1 = \nu_1 RT^2 X_1$$

$$[A13_2] \quad \Delta H_2 = \Delta H_{2(0)} + \bar{L}_2 = \nu_2 RT^2 X_2$$

and in general

$$[A13_n] \quad \Delta H_n = \Delta H_{n(0)} + \bar{L}_n = \nu_n RT^2 X_n.$$

Thus, knowing X_1, X_2, \dots, X_n from eqs. [A8₁] to [A8_n] it is possible to calculate the heats of solutions $\Delta H_1, \Delta H_2, \dots, \Delta H_n$ of components A_1, A_2, \dots, A_n in their saturated multicomponent systems by means of eqs. [A13₁] to [A13_n].

NOTES

ELECTRICAL EFFECTS ON THE C-O-C ASYMMETRICAL STRETCHING VIBRATION IN ANISOLES

G. K. GOLDMAN, H. LEHMAN, AND, C. N. R. RAO*

The infrared vibrational frequencies and the band intensities of several groups in related series of organic molecules have been found to be influenced systematically by substituents (1-4). In benzene derivatives of the type RC_6H_4X , where X is the functional group and R is a meta- or a para-substituent, linear relations have been found between reactivity constants of R with the vibrational frequency of X and also with the logarithm of the band intensity of X (1-4). Among the electron-donating groups, only the hydroxy and the amino groups have been studied in detail. Little is known about the electrical effects of substituents on the ether linkage (C-O-C) in anisoles. The 1200-cm^{-1} band in esters assigned to the C-O stretching vibration has been studied in a number of alkyl esters (5), but the results do not throw any light on the substituent effects. We have now investigated the electrical effects of substituents on the asymmetrical C-O-C stretching vibration (6) in parasubstituted anisoles.

All the compounds were purified before use. The infrared spectra were recorded in carbon tetrachloride solutions using a Perkin-Elmer, Model 21, spectrophotometer. The molarities of the solutions were kept constant at about 0.05 for all the compounds. The apparent molecular extinction coefficients (ϵ) at the maximal frequencies were calculated from the Beer's law.

The C-O-C asymmetrical stretching frequency in *p*-substituted anisoles increases with the electron withdrawing power of the *p*-substituent. The plot of the frequency

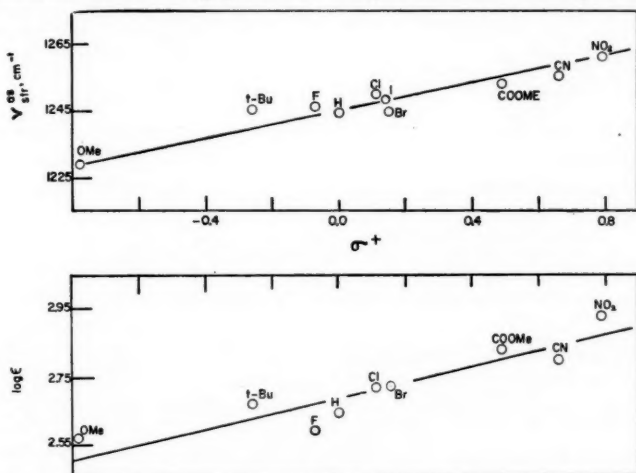
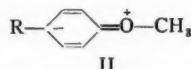
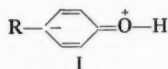


FIG. 1. Correlation of the C-O-C asymmetrical stretching frequency and the band intensity in para-substituted anisoles with the electrophilic substituent constants.

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against Brown- σ^+ values (7) is found to be linear (Fig. 1). The slope of the ν - σ^+ plot is about 21.

The plot of the logarithm of the apparent molecular extinction coefficients of the C-O-C asymmetric stretching frequency against the σ^+ values is also found to be fairly linear (Fig. 1). The band intensity increases with the electron-attracting ability of the p -substituent. The apparent half band widths did not seem to show any regular trend. It is interesting to note that the OH band intensity in substituted phenols also shows a similar behavior (8, 9). Since the band intensity of a stretching vibration is directly related to the electrical properties of the particular bond in question (i.e. bond moment and its direction), it appears reasonable that the prominent resonance structures in phenols (I) and in anisoles (II) should be similar:



The OH stretching frequency in p -substituted phenols (unlike the C-O-C stretching frequency in p -substituted anisoles) decreases with the increasing electron-withdrawing ability of the p -substituent. Of course, it is true that if two functional groups show similar trends of the band intensities with the reactivity constants, it does not follow that the trends of the frequencies will be similar.

ACKNOWLEDGMENT

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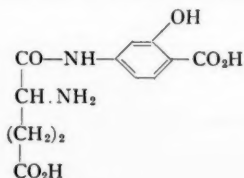
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DERIVATIVES OF p -AMINOSALICYLIC ACID

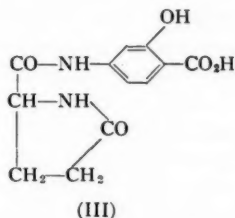
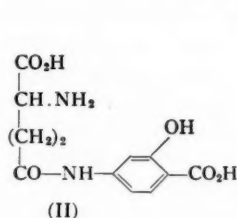
M. H. FISHER AND T. F. MASSIAH

Darrach and Polglase (1) have described the preparation of N-(α -L-glutamyl)- p -aminosalicylic acid (I). They claim that it is a useful antituberculous drug and that it does not cause the toxic side effects associated with p -aminosalicylic acid itself. This report



(I)

describes the synthesis of N-(γ -DL-glutamyl)-*p*-aminosalicylic acid (II) and N-(L-pyrogutamyl)-*p*-aminosalicylic acid (III). The γ -compound (II) was prepared by treatment



of *p*-aminosalicylic acid with N-phthalyl-DL-glutamic anhydride (2), followed by hydrolysis of the intermediate with hydrazine. The reaction of phthalylglutamic anhydride with amines was known to give γ -derivatives (2) and additional evidence for this structure was furnished by the formation of a thiohydantoin when the product was warmed with ammonium thiocyanate and acetic anhydride (3).

The pyroglutamyl-derivative (III) was prepared either by treatment of *p*-aminosalicylic acid with L-pyroglutamyl chloride or by dehydration of N-(α -L-glutamyl)-*p*-aminosalicylic acid when heated above its melting point. Alkaline hydrolysis under a variety of conditions always resulted in cleavage of the side chain amide in preference to the cyclic amide linkage.

EXPERIMENTAL

N-(N-Phthalyl- γ -DL-glutamyl)-*p*-aminosalicylic Acid

A suspension of N-phthalyl-DL-glutamic anhydride (110 g) and *p*-aminosalicylic acid (65 g) in ethyl acetate (2 l.) was stirred at room temperature for 24 hours. The reactants slowly dissolved and then the product separated (120 g) m.p. 227–228° (decomp.). Crystallization from ethyl acetate yielded white needles, m.p. 229° (decomp.). Anal. Calc. for $C_{20}H_{16}N_2O_8$: C, 58.3; H, 3.9; N, 6.8. Found: C, 58.0; H, 4.0; N, 6.7.

N-(γ -DL-Glutamyl)-*p*-aminosalicylic Acid (II)

N-(N-Phthalyl- γ -DL-glutamyl)-*p*-aminosalicylic acid (41.2 g) in 1 *N*-hydrazine hydrate (200 cc) was refluxed for 30 minutes and then cooled. Phthalyl hydrazide was filtered off and the filtrate evaporated to dryness under reduced pressure. The white residue which remained was crystallized from aqueous ethanol yielding the hydrazinium salt of the product (16 g), m.p. 172° (decomp.). Anal. Calc. for $C_{12}H_{18}N_4O_6$: C, 45.9; H, 5.8; N, 17.8. Found: C, 45.9; H, 5.7; N, 17.6.

The salt was treated with 1 equivalent of hydrochloric acid to yield the desired product, m.p. 225° (decomp.). Anal. Calc. for $C_{12}H_{14}N_2O_6$: C, 51.1; H, 5.0; N, 9.9. Found: C, 51.2; H, 5.1; N, 9.9.

1-Acetyl-2-thiohydantoyl-5- β -(3-acetoxy-4-carboxypropionanilide)

A mixture of N-(γ -DL-glutamyl)-*p*-aminosalicylic acid (1 g), ammonium thiocyanate (0.3 g), acetic anhydride (10 cc), and glacial acetic acid (1 cc) was warmed on a hot plate for $\frac{1}{2}$ hour until a clear solution was obtained, and then evaporated under reduced pressure. The residual gum solidified after it was rubbed with water and a little ethanol. Two crystallizations from aqueous ethanol yielded white needles (0.3 g), m.p. 190° (decomp.). Anal. Calc. for $C_{17}H_{17}N_3O_7S$: C, 50.1; H, 4.2; N, 10.3; S, 7.8. Found: C, 49.5; H, 4.2; N, 10.1; S, 7.4.

N-(*L*-Pyroglutamyl)-*p*-aminosalicylic Acid (III)

(a) *L*-Pyroglutamic acid (38.7 g) was added to thionyl chloride (65 cc) and the mixture stirred at room temperature for 5 hours. The excess of thionyl chloride was evaporated under reduced pressure. Dry benzene was added to the residue and then evaporated under reduced pressure to remove the last traces of thionyl chloride. The crude acid chloride was dissolved in tetrahydrofuran (150 cc) and slowly added to a stirred suspension of *p*-aminosalicylic acid (45.9 g) in tetrahydrofuran (150 cc). The mixture was stirred at room temperature for 18 hours, and then the product (76.7 g) was filtered off. Purified material, m.p. 237–238° (decomp.) was obtained by dissolution in aqueous sodium bicarbonate, carbon treatment, and precipitation with hydrochloric acid. Crystallization from water yielded white needles, m.p. 242°–244° (decomp.). Anal. Calc. for $C_{12}H_{12}N_2O_5$: C, 54.6; H, 4.6; N, 10.6. Found: C, 54.7; H, 4.6; N, 10.4. $[\alpha]_D^{21} -7.5^\circ$ (c, 5.0 in water).

(b) *N*-(α -*L*-Glutamyl)-*p*-aminosalicylic acid (4.3 g) was heated at 170° for 4 hours in an oil bath. The starting material melted at 160° and then resolidified. Crystallization from water yielded white needles (1.1 g), m.p. 242–243° (decomp.). The melting point was not depressed by admixture with the product from preparation (a).

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6-*O*-ETHYL-D-GALACTOSE

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In connection with some other work 6-*O*-ethyl-D-galactose was prepared as a sirup by ethylation of 1,2;3,4-di-*O*-isopropylidene-D-galactose followed by dilute acid hydrolysis of the isopropylidene groups. After standing for more than a year at room temperature this new sugar derivative crystallized and the opportunity was taken to record its melting point, equilibrium specific rotation, paper chromatographic behavior, and infrared spectrum.

The 6-*O*-ethyl-D-galactose appeared as a distinct, brown, non-fluorescent spot on paper chromatograms sprayed with *p*-anisidine hydrochloride reagent. This behavior appeared to be characteristic of 6-*O*-alkyl derivatives of galactose since it was shown by 6-*O*-methyl-D-galactose but not by the mono-1,2,3, or 4-*O*-methyl ethers (1). In the glucopyranose series the 2- and 6-mono-*O*-methyl ethers showed this same color reaction which was also distinct from the behavior of the 3- and 4-*O*-methyl compounds (2).

EXPERIMENTAL

Paper chromatograms were prepared with 1-butanol-ethanol-water (5:1:4 v/v) and were sprayed with *p*-anisidine hydrochloride reagent.

6-*O*-Ethyl-1,2;3,4-di-*O*-isopropylidene-D-galactose

Diacetone-D-galactose (1,2;3,4-di-*O*-isopropylidene-D-galactopyranose) was prepared from D-galactose in 34% yield (3), $[\alpha]_D^{20} -55.0^\circ$ (c, 6.66 in chloroform) and gave a single

yellow spot, R_f 0.88, on a paper chromatogram. A mixture of diacetone-D-galactose (5.04 g), acetone (10 ml), water (25 ml), and sodium hydroxide pellets (10 g) was heated to 55° C with vigorous stirring, and diethyl sulphate (13 ml) was added dropwise over a period of 45 minutes. The mixture was then heated at 85° C for 1 hour, cooled, and extracted with chloroform. The chloroform extract was dried (anhydrous sodium carbonate) and evaporated and the residue was distilled under reduced pressure from sodium carbonate (yield, 3.68 g, 66%). Hydrolysis of a sample with boiling 70% acetic acid and paper chromatography of the hydrolyzate showed that the sirupy distillate contained some unreacted diacetone-D-galactose. The developed chromatogram had a distinct, brown, non-fluorescent spot, R_f 0.40, for 6-O-ethyl-D-galactose plus a faint, yellow-brown, fluorescent spot, R_f 0.11, which corresponded to D-galactose. The sirup was redistilled from sodium hydroxide (b.p. 101–103° C at 0.2 mm) to give 2.63 g of a colorless product, $[\alpha]_D^{27} -57.6^\circ$ (c , 4.90 in ethanol), which failed to crystallize.

6-O-Ethyl-D-galactose

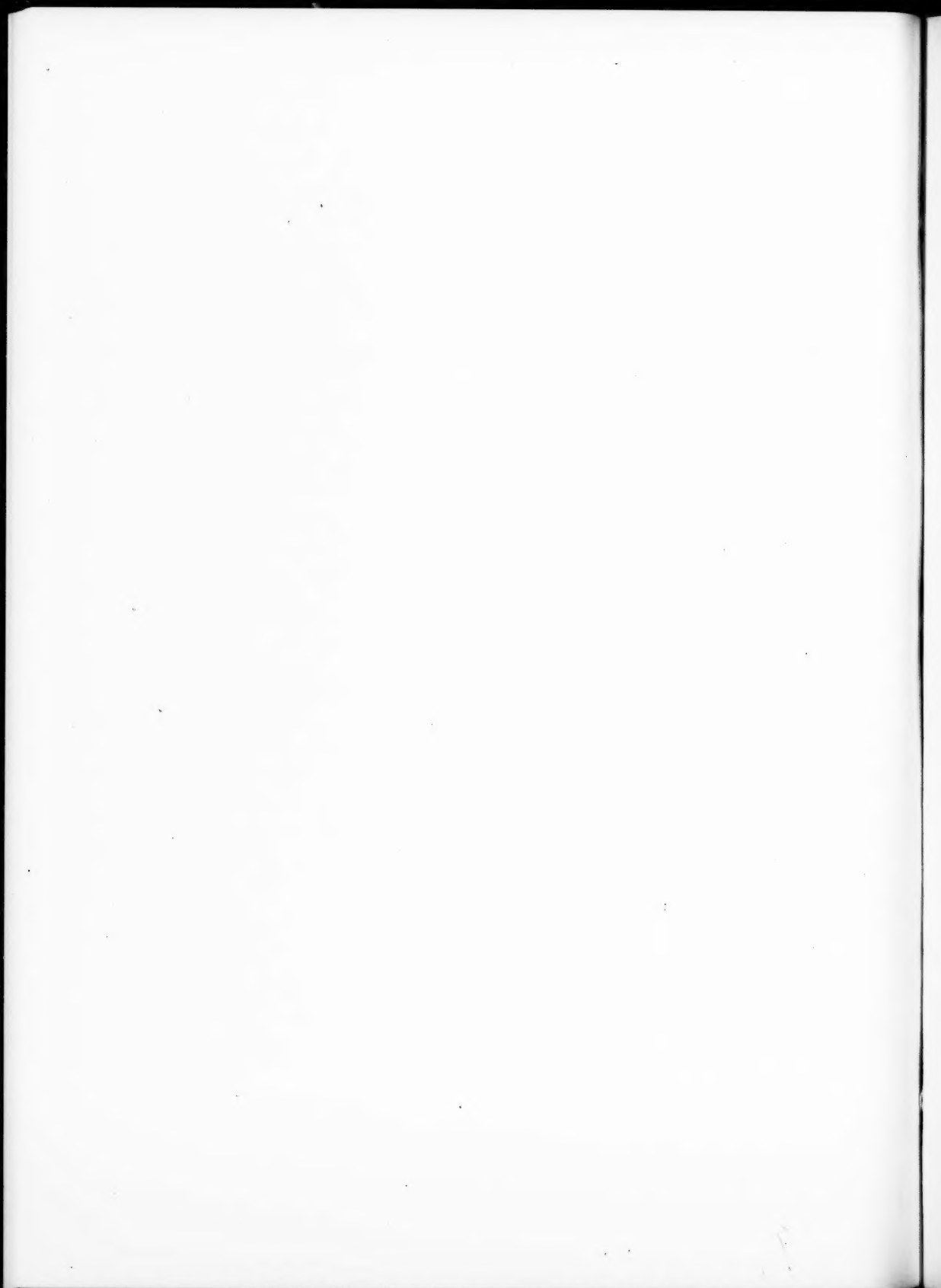
6-O-Ethyl-1,2;3,4-di-O-isopropylidene-D-galactopyranose (783 mg) was dissolved in 80% acetic acid (10 ml) and heated on a steam bath for 15 hours. The hydrolyzate was evaporated to dryness *in vacuo* and the residue was refluxed with water (10 ml) for 5 hours to reverse any acetate formation. A chromatogram showed a trace of D-galactose in the product which was removed by passage through a cellulose column developed with butanol–water. The appropriate fractions when combined yielded a colorless glass (358 mg, 63.3%) which crystallized in pentagonal plates after standing at room temperature for 15 months. The reducing sugar derivative was recrystallized from anhydrous ethyl acetate to a constant melting point (104.5–105.0° C); $[\alpha]_D^{27} +88.6^\circ$ (23 minutes) changing to $+69.0^\circ$ (constant at 148 minutes) (c , 2.10 in water). Anal. Calc. for $C_{18}H_{28}O_8$: C, 46.1; H, 7.7; OC_2H_5 , 21.6%. Found: C, 45.8; H, 7.5; OC_2H_5 , 21.8%.* The infrared spectrum of the compound (potassium bromide window) exhibited absorption maxima at the following frequencies (cm^{-1}): 3430, 2900, 1635, 1390, 1240, 1100, 970, 830, 800, 775.

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*Microanalyses by A. Bernhardt, Kaiser Wilhelm Platz, Mulheim (Ruhr), Germany.



NOTES TO CONTRIBUTORS

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Contents

<i>J. H. Robson and George F Wright</i> —The mechanism of organomercurial oxidation by mercuric salts - - - - -	1
<i>J. H. Robson and George F Wright</i> —The autooxidation of organomercuric salts - - - - -	21
<i>C. Brissette and C. Sandorfy</i> —Hydrogen bonding in the amine hydrohalides. II. The infrared spectrum from 4000 to 2200 cm^{-1} - - - - -	34
<i>M. W. Lister and Y. Yoshino</i> —Complex cobalt periodates - - - - -	45
<i>A. F. Sirianni, F. W. Meadus, and I. E. Puddington</i> —Some properties of silica dispersions - - - - -	53
<i>Wendell J. Biermann</i> —The relative enthalpies of concentrated potassium hydroxide solutions - - - - -	57
<i>P. J. Dyne and J. M. Kennedy</i> —A detailed study of the Samuel-Magee model for the radiation chemistry of water. Part II. Kinetics of radical reactions in the tracks of densely ionizing particles - - - - -	61
<i>R. J. Woods and J. W. T. Spinks</i> —The radiolysis of some organic halogen compounds in aqueous solution - - - - -	77
<i>L. Ross C. Barclay, J. W. Hilchie, A. H. Gray, and (in part) N. D. Hall</i> —Cyclalkylations of alkyl benzenes with olefins and alkyl halides - - - - -	94
<i>G. Giacometti, H. Okabe, S. J. Price, and E. W. R. Steacie</i> —The photolysis and the fluorescence of perfluoro diethyl ketone - - - - -	104
<i>T. J. Painter</i> —The polysaccharides of <i>Furcellaria fastiglata</i> . I. Isolation and partial mercaptolysis of a gel-fraction - - - - -	112
<i>M. A. A. Beg and H. C. Clark</i> —Chemistry of the trifluoromethyl group. Part I. Complex formation by phosphines containing the trifluoromethyl group - - - - -	119
<i>James B. Hyne</i> —Hydrogen bonding in diastereoisomeric α - β aminoalcohols: a reinvestigation of the ephedrine by N.M.R. - - - - -	125
<i>R. A. Abramovitch and A. M. Marko</i> —The structure of 2- <i>p</i> -dimethylamino-benzylideneindoxyl and its salts - - - - -	131
<i>R. U. Lemieux and A. G. McInnes</i> —The preferential tosylation of the <i>endo</i> -5-hydroxyl group of 1,4;3,6-dianhydro-D-glucitol - - - - -	136
<i>D. Basmadjian</i> —Adsorption equilibria of hydrogen, deuterium, and their mixtures. Part I. - - - - -	141
<i>D. Basmadjian</i> —Adsorption equilibria of hydrogen, deuterium, and their mixtures. Part II. - - - - -	149
<i>P. A. D. de Maine and P. J. Santiago</i> —Iodine complexes in inert solvents. XI. Cryoscopic study of the iodine-naphthalene complex dissolved in cyclohexane - - - - -	157
<i>Y. Iyengar</i> —Calculation of heats of solution in saturated mixed electrolytes - - - - -	161
Notes:	
<i>G. K. Goldman, H. Lehman, and C. N. R. Rao</i> —Electrical effects on the C-O-C asymmetrical stretching vibration in anisoles - - - - -	171
<i>M. H. Fisher and T. F. Massiah</i> —Derivatives of <i>p</i> -aminosalicylic acid - - - - -	172
<i>G. G. McKeown and L. D. Hayward</i> —6-O-ethyl-D-galactose - - - - -	174

